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KINETIC ISOTOPE EFFECT ON DEUTERIUM AND TRITIUM EXCHANGE IN LIQUID AMMONIA

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This work deals with the mechanism of isotopic exchange of hydrogen with a base. Measurement of the kinetics of exchange of deuterium and tritium in fluorene and methyl β-naphthyl ketone with liquid ammonia showed that the ratio of rate constants $k_D/k_T = 2$. A positive isotope effect is also observed in the metalation of aromatic substances by organoalkali compounds. Comparison of the regularities of reactions of isotopic exchange of hydrogen with a base and metalation reactions; in particular, comparison of the influence of the isotope mass on the rates of these reactions, indicates that their mechanisms are similar. The reaction rate is limited by the process of C–H bond cleavage on attack of the hydrogen atom by the base.

Study of the kinetic isotope effect (KIE) may facilitate understanding of the reaction mechanisms by giving some indications with regard to the rate-limiting stage, the structure of the transition state, and the character of the bonds therein. The kinetic isotope effect is most pronounced when hydrogen isotopes are used, since their point energies of the bonds between a given element and different hydrogen isotopes are considerably different. Valuable information on isotope effects in hydrogen-substitution and migration reactions has been obtained by means of such isotopes (see reviews [1-7]).

As is well known [8], hydrogen exchange serves as a model for more complex hydrogen-substitution reactions. Thus there is a close similarity between the regularities of electrophilic hydrogen substitution in aromatic compounds (nitration, halogenation, etc.) and hydrogen exchange with acids. The same may be said about reactions of metalation of organic substances by organoalkali compounds in comparison with hydrogen exchange with bases.

Melander and Olsson [9, 10] measured the ratio of the rate constants of isotopic exchange of deuterium- and tritium-substituted toluene and benzene with ordinary sulfuric acid in heterogeneous systems and thus determined the KIE in acid hydrogen exchange for the first time.

A work on the comparison of the rates of isotopic exchange of deuterium and tritium in fluorene with a base–liquid ammonia–has been briefly reported [11]. Similar measurements were carried out [12] on the reaction between liquid ammonia and isotope-substituted methyl β-naphthyl ketone. The results of investigation of the kinetic isotope effect in deuterium and tritium exchange for the indicated substances in liquid ammonia are set forth in the present article.

EXPERIMENTAL

Preparation of Compounds. Fluorene containing a heavy hydrogen isotope in the methylene group was prepared by treatment of fluorenyllithium, synthesized by the method given in [13], with D_2O or HTO. Part of the experiments in deuterium exchange were performed with fluorene in which a CH_2-group hydrogen was replaced by deuterium through isotopic exchange between deutero-ammonia and ordinary fluorene. M.p. 115°.

Methyl β-naphthyl ketone with the heavy isotope in the methyl group, was prepared through the exchange reaction between the ordinary ketone and a 1 N KOH solution in D_2O or HTO at a temperature near 90°. M.p. 53.7°.

Performing of Experiments in Isotopic Exchange. Employing the usual procedure for work with liquefied gases under pressure [14], 11-13 g of carefully dried liquid ammonia, whose temperature had been brought to 25°, was added to 0.1-0.2 g of the substance. An ampule containing the reaction mixture was placed in a thermostat (25 ± 0.02°). The exchange reaction was stopped by cooling the reaction mixture to -78° or pouring it into ice water. The substance was isolated, purified, and ignited in a stream of oxygen, and the purified water from the ignition was analyzed for deuterium and tritium, respectively. The deuterium concentration was determined by the drop method [15], with 1-2% accuracy. The procedure for tritium determination is described below.

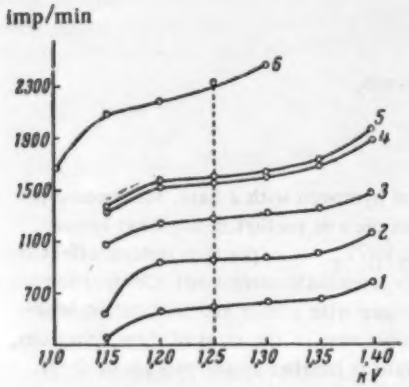

Fig. 1. Characteristic counter curves at various pressures (mm Hg) of the mixture: $HT + H_2$, having constant specific activity. 1) 0.98; 2) 1.80; 3) 2.36; 4) 2.82; 5) 3.08; 6) 4.64.

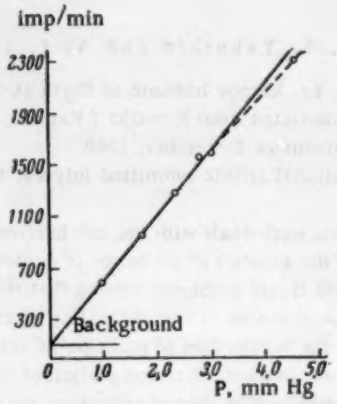

Fig. 2. Activity of tritium as a function of the pressure of $HT + H_2$ in the counter.

Tritium Determination. The water from ignition of the substance was decomposed by zinc dust under unvarying conditions at 410° by a method similar to that described in [16, 17]. The isotope-fractionation effect was held constant. To hydrogen containing tritium (pressure 1-4 mm, measured with an accuracy of ± 0.01 mm), purified commercial n-butane was added (pressure 20 mm). An SBM-7 or SBS-5 counter was filled with this mixture.

A better counting characteristic is obtained by filling the counter with tritiated butane prepared through the reaction of butylmagnesium bromide with tritiated water [18] than by filling it with the indicated mixture, namely, a 400 v "plateau" with a slope less than 1% per 100 v. However, this method of analysis involves certain experimental difficulties and takes considerable time.

The presence of hydrogen in the mixture with butane degraded the counting characteristic in our experiments by shortening the "plateau" to 150-200 v, or even further at a hydrogen pressure above 5 mm. In Fig. 1 are given characteristic curves for mixtures containing increasing amounts of hydrogen with a constant amount of butane (20 mm). In Fig. 2, on the basis of the same measurements, it is shown how the number of impulses per minute depends on the hydrogen pressure in the mixture with butane, filling the counter. In the 1-4 mm pressure range the points lie quite close to a straight line, whereas deviation from linearity is observed as the hydrogen pressure is raised above 4 mm.

In Table 1 are given the results of measurements of the activity of water samples obtained by diluting a stock sample of tritiated water (10^{-3} curie/liter) in which the tritium content was taken to be 100%. Each measurement was repeated several times. The quantity Δ—the average deviation from the average activity in imp/min·mm—and the same error in percentages of the quantity being measured are also indicated in the table.

Average values of the specific activity of each water sample are plotted against the relative tritium concentration (C_{HTO}) in Fig. 3. The points fall on a straight line; i.e., the number of impulses (corrected for background) actually is directly proportional to the tritium concentration in the water.

TABLE 1.

Specific Activity of Hydrogen as a Function of the Tritium Concentration in Water

C_{HTO}	HT, imp/min·mm	Δ, imp/min·mm	Δ, %
100	3067	64	2
80	2452	70	3
50	1528	20	1
30	919	13	1

In addition, in order to judge the accuracy of the measurements, we give the results of parallel analyses of the tritium content in a single sample of tritiated methyl β-naphthyl ketone.

imp/min·mm	670	645	647	681	635	Average	655
Δ,imp/min·mm	19	6	4	30	16	Average	15

It should be noted that after each activity measurement the counter was evacuated, filled with butane, and again evacuated to a vacuum of about 10^{-4} mm, being simultaneously heated at 200°. After this the "background" (about 100 imp per min) remained constant (there was no "memory effect").

The results set forth show that the analytical errors amounted to 2-3% of the measured quantities. In principle, the accuracy could be increased by improving the method of preparing the gas to be determined from water.

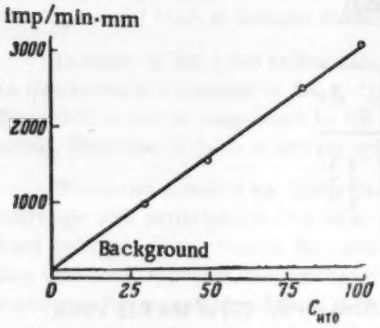

Fig. 3. Specific activity of tritium in water samples containing different initial amounts of radioactive water (C_{HTO}). Each point is the result of several parallel measurements.

Results of Measurements

The results of the measurements of isotopic-exchange kinetics are given in Table 2-5. The following symbols are used: τ – the duration of the experiment, sec; C_0 – the concentration of the heavy isotope in the water from ignition of the substance before the experiment; C_τ – the same at the instant of completion of the experiment; k_D and k_T – rate constants of deuterium and tritium exchange, calculated by a first-order equation.

The rate constants for deuterium exchange in fluorene and methyl β-naphthyl ketone at 25° are close to those determined earlier [19-21].

	$k_D \cdot 10^5$	$k_T \cdot 10^5$	k_D/k_T
Fluorene	16 ± 0.1	8.3 ± 0.1	1.9
Ketone	8.0 ± 0.1	3.7 ± 0.2	2.2

The following rate constants for tritium exchange were established: fluorene – $(8.3 \pm 0.1) \cdot 10^{-4}$ sec^{-1}; ketone – $(3.7 \pm 0.2) \times 10^{-5}$ sec^{-1}.

Let us compare the average values of the rate constants of deuterium and tritium exchange for the two substances*:

TABLE 2.

Experiments in Exchange of D-Fluorene

τ, sec	C_0	C_τ	$k_D \cdot 10^4$	τ, sec	C_0	C_τ	$k_D \cdot 10^4$
5400	4,56	1,78	1,7	5400	4,56	2,03	1,5
5580	4,56	1,51	1,9	7800	4,56	1,36	1,5
5400	4,56	1,88	1.6	7380	4,56	1,38	1,6
7200	4,56	1,27	1,8	5400	9,14	4,00	1,6
7200	4,56	1,38	1,7	5400	9,14	3,97	1,6
5400	4,56	2.17	1,4				

	Fluorene	Ketone
Present work	$(1.6 \pm 0.1) \cdot 10^{-4}$ sec^{-1}	$(8.3 \pm 0.4) \cdot 10^{-5}$ sec^{-1}
Work (19)	$2 \cdot 10^{-4}$	
Work (20,21)	$1.7 \cdot 10^{-4}$	$(8.0 \pm 0.1) \cdot 10^{-5}$

Thus, for the substances investigated, deuterium bound to aliphatic carbon exchanges with the protium of liquid ammonia at 25° twice as rapidly as tritium. This is the principal result obtained in the present work.

*A value of the rate constant, taken from [20], was adopted for the ketone.

TABLE 3.

Experiments in Exchange of T-Fluorene

τ, sec	C_0	C_τ	$k_T \cdot 10^8$
3600	772	574	8,1
5400	772	543	(6,5)
5400	730	457	8,5
3600	730	529	8,4
3600	730	539	8,3
5400	730	455	8,5

TABLE 4.

Experiments in Exchange of D-Methyl β-Naphthyl Ketone

τ, sec	C_0	C_τ	k_D 10^8
7200	4,69	2,25	9
7200	4,69	2,38	8
5400	4,69	3,01	8

TABLE 5.

Experiments in Exchange of T-Methyl β-Naphthyl Ketone

τ, sec	C_0	C_τ	k_T 10^8	τ, sec	C_0	C_τ	k_T 10^8
3600	655	577	3,4	5940	655	507	4,1
6600	655	515	3,6	5280	655	535	3,7
5400	655	543	3,5	5220	655	541	3,7
5520	655	517	4,1				

RESULTS

The indicated result agrees with the conclusions of theoretical calculations [9, 22, 23] of the KIE which show that at room temperature the C–D bond should be cleaved about two to three times as rapidly as the C–T bond. The theoretical estimate is very approximate and, in particular, does not take into account those differences which may be caused by dissimilar bond polarization in the transition state. Hence the experimental determination of kinetic isotope effects for different reactions carried out under different conditions is of great interest.

Recently Streitwieser [24] obtained $k_D/k_T=3.0\pm0.3$ for the isotopic exchange reaction of the heavy isotope in the nethylene group of ethylbenzene; the reaction catalyst was lithium cyclohexylamide in cyclohexylamine (49.9°). In the same note there is a reference to similar unpublished work by Langworth, according to which $k_D/k_T=2.75$; 2.98 for substitution of deuterium and tritium in the methyl group of toluene.

Thus, hitherto-known values of k_D/k_T, found by comparing the kinetics of exchange of deuterium and tritium bound to a carbon atom with the protium of a base, lie within the limits of a theoretical estimate of the effect, based on the hypothesis that the stage of cleavage of the bond with carbon in the transition state limits the reaction rate; the tunnel effect is negligible in the case of heavy hydrogen isotopes, especially tritium, although its presence must be taken into account in reactions in which ordinary hydrogen takes part [6, 25].

The great similarity between the regularities of reactions of hydrogen exchange with bases and those of metalation reactions between organic compounds and organoalkali reagents was mentioned at the beginning of the article. This also applies to the KIE. Actually Bryce-Smith, Gold, and Satchell [26] found a positive KIE on measuring the rate of metalation of ordinary and deuterated benzene and toluene by ethylpotassium, and also noted how the magnitude of the effect depends on temperature. Gronowitz and Halvarson [27] found that tritiated thiophene is metalated by butyllithium one-sixth as rapidly as ordinary thiophene.

At present only more or less probable assumptions can be made with regard to the structure of the transition state in the hydrogen-substitution reactions being discussed. However, all the data known today, which are analyzed in detail in monograph [8], lead to the conclusion that both reactions take place through attack of the C–H bond hydrogen atom by the base, as in other reaction between bases and carbo acids. This conclusion received additional support in works of our laboratory [28-30], which demonstrated the direct relation between the partial rate of substitution of hydrogen ortho atoms in benzene derivatives and the degree of acidity of the corresponding C–H bonds.

Data on the KIE in hydrogen exchange with bases and in metalation are in full agreement with the idea that in these reactions the rate is limited by the stage of cleavage (or elongation) of that CH bond in the organic molecule which takes part in the transition state.

The fact that a positive KIE exists is not in itself enough to draw a definite conclusion on the reaction mechanism in detail. For instance, according to Melander and Olsson's measurements [9, 10], $k_D/k_T = 1.7$ for acid hydrogen exchange in benzene and toluene, whereas according to Gold, Lambert, and Satchell's determination [31] $k_D/k_T = 2\text{-}3$ for replacement by protium of hydrogen isotopes in the aromatic ring of o-cresol in solutions of equal acidity. The authors of each work hold that the result obtained satisfies the exchange-reaction scheme adopted by them, but does not contradict the competing scheme.

Melander and Olsson, on the basis of the usual treatment of the mechanism of electrophilic hydrogen substitution, assume that the exchange reaction takes place according to a two-stage scheme. Its first stage consists in the addition of a proton to an aromatic-ring carbon atom bound to a deuterium (or tritium) atom. A σ-complex is formed, in which atoms of two isotopes are bound to the same carbon atom. Cleavage of the bond to the isotope atom originally present in the molecule takes place in the transition state, which is similar in structure to the σ-complex and leads to isotopic exchange.

Contrary to the cited authors, Gold, Lambert, and Satchell assume that in the course of acid isotopic exchange an intermediate compound of the π-complex type arises, in which the bonds to the two isotopes are unsymmetrical. The reaction rate is determined by the stage in which the isotope atoms change places in the intermediate compound. Then one of them is quickly split off in the form of a positive ion; the result of this is isotopic exchange.

These two schemes are dissimilar, and at the same time differ from the scheme adopted by us for isotopic exchange with participation of a base, where it is assumed that the attack of the reagent is directed to the C–H bond hydrogen atom, whereas the carbon atom of this bond, or the aromatic ring as a whole, takes part in the reaction with acid. However, we concluded that, despite the difference in the mechanisms of acid and basic hydrogen exchange, the magnitude of the KIE is nearly the same in both cases.

To illustrate further the proposition that data obtained in the study of the KIE are not enough in themselves to draw unambiguous conclusions on the reaction mechanism, we also cite the views of Hammond [32]. In his opinion, even the absence of a positive KIE does not by any means always permit the categorical exclusion of bond cleavage in the stage controlling the reaction rate. The case of an immeasurably small KIE may occur if the potential curve of the reaction in which the intermediate compound is formed has potential barriers of nearly the same height on both sides of the minimum.

E. A. Shilov and F. M. Vainshtein [33] also do not regard the absence of a KIE in electrophilic hydrogen substitution as unambiguously proving that the reaction rate is not limited by the stage in which the proton is broken off. The authors showed experimentally that in the iodination and bromination of aromatic compounds the KIE may have various values, including zero, depending on the substrate and reagent used. The value of the KIE is also influenced by the pH of the reaction medium.

Melander and Olsson [9, 10] compared KIE values for deuterium and tritium substitution in benzene and in various positions of the aromatic ring of toluene, and noticed a decrease in the ratio k_D/k_T with decrease of reactivity of the bond at which the substitution takes place. This conclusion was confirmed [34] in a study of acid hydrogen exchange in thiophene.

Sulfuric acid, a reagent which levels out the differences in reactivity of nonequivalent positions in the aromatic ring, took part in exchange reactions, as may be seen on considering the relation between the partial rate of acid hydrogen exchange and its selectivity [8, 35]. Since it is known that nonequivalent positions are especially strongly differentiated with respect to reactivity in hydrogen exchange with liquid hydrogen bromide, it is expedient to use the latter for a more detailed study of the phenomenon discovered by Melander and Olsson.

In future work we propose to continue our measurements of the KIE in basic hydrogen exchange, along lines suggested by the idea of the probable influence of bond character (bond polarity) in the transition state on the value of the KIE, using various protophilic solvents and catalysts.

SUMMARY

1. The kinetics of isotopic exchange of deuterium and tritium in fluorene and methyl β-naphthyl ketone with liquid ammonia was measured at 25°. It was shown that in both cases deuterium exchanges with protium twice as rapidly as tritium.

2. The results obtained are compared with data on the kinetic isotope effect (KIE) in metalation reactions between organic substances and organoalkali compounds, since the regularities of both types of reactions are similar. The presence of a positive KIE in the reactions named, together with other information on their peculiarities, fully agrees with the hypothesis that in these reactions the rate is controlled by the stage of cleavage (or elongation) of a C–H bond in the molecule on attack of the hydrogen atom of the C–H bond in the transition state by the base.

3. It was found that values of the KIE for hydrogen exchange reactions both with bases and acids studied up to now are nearly the same, although the mechanisms of these reactions are different in detail.

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THE ORIGIN OF THE COMPENSATION EFFECT IN RADIATION-INDUCED RADICAL RECOMBINATION IN POLYMERS

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By analyzing experimental data on the reaction rate constants for radical recombination in irradiated polymers it has been found that lg k^0 and E are connected by a linear relation (compensation effect) and that abnormally high (up to 10^{+6} cm^3/sec) pre-exponential factors occur. It has been proposed that the activation energy is lowered when the temperature increases (in the range close to the melting point of the polymer). It has been shown that this assumption enables us to explain the abnormally high values of the pre-exponential factors as well as the compensation effect.

When measuring the recombination rate constants of fluoralkyl and peroxide radicals in irradiated polytetrafluorethylene (teflon) we have discovered [1] that, depending upon the crystallinity (α) of the sample, the zones in which the radicals are found and the radical species (R or RO_2), the pre-exponential factors (k^0) and the activation energies (E) vary over a very broad range (E from 10 to 65 kcal/mole, k^0 from 10^{-16} to 10^{+6} cm^3/sec). At the same time there is found a good linear relation between lg k^0 and E. An analysis of data from the literature [2-4], which has been carried out in the paper [1] mentioned above, has shown that an analogous picture is also observed for recombination reactions in hydrocarbon polymers (for which experimental data exist). Data on rate constants of radical recombination in hydrocarbon polymers, polyvinylchloride and various teflon samples are given in Table 1. The unusually high values of the pre-exponential factor for fluoralkyl and alkyl radical recombination immediately attract attention. As is well known, the values of the pre-exponential factor for bimolecular reactions in gases or liquids lie in the range 10^{-10}-10^{-15} cm^3/sec. Few reaction rate constants have been measured in the solid state, but, obviously, their pre-exponential factor should be still smaller [5-7]. Approximative calculations show that the various complex kinetic mechanisms which result in a quasi-bimolecular over-all reaction, even when the entropy term is taken into account, cannot raise the pre-exponential factor by more than 5-6 orders of magnitude, so that pre-exponential factors between 10^{-3} and 10^{+6} cm^3/sec, as are found for radical recombination in polymers, require a special explanation.

As can be seen in Fig. 1, the points for the various teflon samples and those for hydrocarbon polymers, when plotted in the coordinates lg k^0 – E, neatly lie on straight lines. The existence of such a relation between k^0 and E is known under the name of compensation effect (KEF) and is characteristic for a great number of chemical reactions in the solid state [8-10] and physical phenomena (gas diffusion in solids [10], viscosity [10], electrical conductivity in semiconductors [10, 11]). Although this effect had been discovered experimentally very long ago, up to now a theoretical explanation is missing. In a recent paper [12] Roginskii and Khait prove that a compensation effect is theoretically possible for reactions in the solid state; however, the relation between k^0 and E which they have obtained cannot satisfactorily explain the experimental results given in Fig. 1 and Table 1. Firstly, according

to Roginskii, lg k^0 should be proportional to E^2, whereas Fig. 1 shows that the points in a broad range neatly satisfy a linear relation between lg k^0 and E. Secondly, an analysis of function $k^0(E)$ obtained in the paper cited indicates that this theoretical relation cannot explain pre-exponential factors raised by more than 6-8 orders of magnitude (above normal values), whereas values differing from normal ones by 10-20 orders of magnitude are found experimentally.

TABLE 1.

Observed k^0_{eff} and E_{eff} values for radical recombinations in polymers

Polymer No.	Polymer	Recombination temperature	k_{eff}, cm^3/sec	E_{eff}, kcal/mole	T_g,°C
1	Polymethylmethacrylate	30–55	10^{-3}	28	90
2	Polyvinylchloride	70–100	0.7	38	90
3	Polyethylene	40–100	10^{+3}	38	100
4	High pressure polyethylene	40–100	1	32	
5	Polypropylene	20–80	10^{-6}	23	160
	Teflon (Ṙ)				
6	α-74%, crystalline phase	220–270	10^{+6}	35±5	307
7	α-46%, "	200–220	10^{-3}	40±4	
8	α-46%, amorphous phase	180–220	10^{-7}	30±3	170
	Teflon ($\dot{R}O_2$)				
9	α-74%, crystalline phase	160–200	10^{-10}	26±3	307
10	α-46%, amorphous phase	140–180	10^{-8}	26±3	
11	α-74%, "	120–200	10^{-16}	10±2	170
12	α-46%, "	110–180	10^{-15}	12±2	

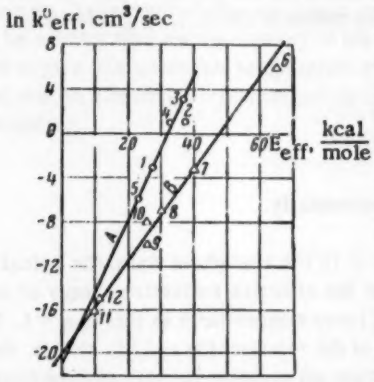

Fig. 1. The logarithm of the pre-exponential factor plotted versus the activation energy for radical recombination in polymers: A) hydrocarbon polymers; B) teflon. The numbering of the points corresponds to the polymer No. in Table 1.

At present it may be considered as already established that the activation energy of free radical recombination in irradiated polymers is determined by the potential barrier hindering the rotation of the polymer chain segments [3,13] and consequently not by the structure or the properties of the radicals, but by the structure of the entire polymer. Independent measurements indicate that the height of the potential barrier hindering the rotation of the polymer chain segments in various polymers lies in the range 10-25 kcal/mole [3, 13, 14]. As can be seen in Table 1, activation energies of about this magnitude are observed in those cases where the pre-exponential factor has a normal value (10^{-10} - 10^{-15} cm^3/sec). In our opinion, the entire set of facts reported may be explained by assuming that, in the range where recombination takes place the activation energy drops at increasing temperatures as a result of some phase changes in the crystal structure. In fact, recombination of radicals is generally observed at temperatures close to the melting point of the polymer. At such temperatures a reorganization of the structure may take place and result in lowering the potential barriers which hinder the various movements of the chain segments, since, obviously, in a completely melted polymer such barriers cannot be too high and the melting process in polymers is spread out over a rather broad temperature range. It is interesting to remark that in nearly all polymers mentioned in Table 1 sharp changes in the mechanical properties (dynamic elasticity modulus, tangent of the loss angle and so on [14]), which are always connected with phase changes, are also found in the vicinity of the temperature range in which the recombination is observed. The temperatures (T_g) at which the former changes are found have been given in the last column of Table1. So, from the viewpoint of physical conceptions our assumption may be considered as justified.

We will carry out some quantitative estimates. If the activation energy depends upon the temperature, that is, if:

$$k = k_0 \exp\left\{-\frac{E(T)}{RT}\right\},$$

then the effective activation energy at a certain mean temperature, when determined in the usual way, will be equal to

$$E_{eff} = RT^2 \frac{\partial \ln k}{\partial T} = RT^2 \frac{\partial}{\partial T}\left[\ln k^0 - \frac{E(T)}{RT}\right] =$$
$$= RT^2\left[\frac{1}{RT^2}E(T) - \frac{1}{RT}\frac{\partial E}{\partial T}\right] = E(T) - T\frac{\partial E(T)}{\partial T}.$$

Similarly, the effective pre-exponential factor at the temperature T can be derived in the following way:

$$\ln k = \ln k^0_{eff} - \frac{E_{eff}}{RT} = \ln k^0 - \frac{E}{RT} =$$
$$= \ln k^0 - \frac{E_{eff} + T\frac{\partial E}{\partial T}}{RT} = \ln k^0 - \frac{1}{R}\frac{\partial E}{\partial T} - \frac{E_{eff}}{RT},$$

from which one obtains that $\ln k^0_{eff} = \ln k^0 - \frac{1}{R}\frac{\partial E}{\partial T}$.

So, the effective values of E_{eff} and k^0_{eff} which we have determined from the experimental data are connected with the actual activation energies and pre-exponential factors by means of the following relations:

$$E_{eff} = E - T\frac{\partial E}{\partial T}, \qquad (1)$$

$$k^0_{eff} = k^0 \exp -\frac{1}{R}\frac{\partial E}{\partial T}. \qquad (2)$$

Since $\frac{\partial E}{\partial T} < 0$, it follows that $E_{eff} > E$ and $k^0_{eff} > k^0$, as is found experimentally.

We suppose that in each teflon sample, be it in the crystalline or in the amorphous state, the actual activation energy of fluoralkyl radical recombination is equal to or close to the effective activation energy of peroxide radical recombination, since the latter recombination takes place at lower temperatures so that $E_{eff} \simeq E$. Then $\partial E/\partial T$ and k^0 for the former recombination can be found by means of the relations (1) and (2), that is, the actual pre-exponential factor can be calculated. The results of this calculation are given in Table 2. As is obvious from the last but one column of Table 2, the actual values of the pre-exponential factor fall into the range of the normal values (10^{-9}-10^{-16} cm^3/sec); in all cases they are close to the corresponding ones for $\dot{R}O_2$. So, our assumption explains the experimental data on teflon, at least as regards the order of magnitude.

If it is supposed for the other polymers listed in Table 1 that the actual E lies in the range 10-20 kcal/mole, then the pre-exponential factors are also lowered to normal values.

Starting from the assumptions mentioned above we show in Fig. 2 how the activation energy of fluoralkyl radical recombination will approximately depend upon temperature. From (1) it follows that the effective value of the activation energy is determined by the point where the tangent to the E(T) curve intersects the ordinate axis.

The question arises whether the proposed mechanism, according to which E is lowered at increasing temperature and E_{eff} is raised, can agree with the fact that Arrhenius' law is found to be valid for the experiments in a rather broad temperature range. It can easily be seen that, if E is a linear function of T (E = A-BT), Arrhenius'

law is still exactly observed where $E_{eff} = A$, $k^0_{eff} = k^0 e^{+B/R}$. Since our measurements are carried out with some inaccuracy, the actual dependency of E upon T may even be not linear, it must only be sufficiently smooth.

TABLE 2.

Estimate of the actual k^0 values for the recombination of fluoralkyl radicals in teflon

Sample		Mean temperature, T° K	E_{eff} from data on R	E from data on $\dot{R}O_2$	mean of $\frac{dE}{dT}$, $\frac{kcal}{mole\ deg}$	k^0_{eff}, cm^3/ /sec	k^0_{eff}/k^0	k^0, cm^3/ /sec	k^0 from data on $\dot{R}O_2$
α, %	phase								
74	Crystalline	520	65	26	77	10^6	10^{17}	10^{-11}	10^{-10}
46	The same	485	40	26	27	10^{-3}	10^6	19^{-9}	10^{-8}
46	Amorphous	476	30	10	42	10^{-7}	10^9	10^{-16}	10^{-15}

In fact, if the activation energy depends on temperature approximately as is depicted in Fig. 2 (curve 1), then it can easily be shown that in the temperature range used the deviation from Arrhenius' law may remain unnoticed. The change in the effective activation energy in a small temperature range δT is equal to

$$\delta E_{eff} = \delta E - \delta\left(T\frac{\partial E}{\partial T}\right) \delta E - \frac{\partial E}{\partial T}\,\delta T - T\,\frac{\partial^2 E}{\partial T^2}\,\delta T,$$

so $\delta E = \frac{\partial E}{\partial T}\,\delta T$, so that

$$\delta E_{eff} = -T\delta T \cdot \frac{\partial^2 E}{\partial T^2},$$

$$\frac{\partial^2 E}{\partial T^2} = -\frac{\delta E_{eff}}{T\delta T}. \qquad (3)$$

Formula (3) determines the maximum curvature of the E(T) curve for which the deviation from Arrhenius' law will be smaller than the inaccuracy of the measurements. We will show that such a curvature is formally sufficient to give in a reasonable temperature range ΔT(~200°) a lowering of the activation energy by 26 kcal/ /mole (a) and an effective activation energy increased to 65 kcal/mole (b). To carry out these two estimates we use the relations:

$$\Delta E \simeq -2\left(\frac{\partial^2 E}{\partial T^2}\right)(\Delta T)^2, \qquad (a)$$

$$\frac{\partial E}{\partial T} \simeq -2\left(\frac{\partial^2 E}{\partial T^2}\right)\Delta T. \qquad (b)$$

Applying (3) we obtain two conditions for the temperature range in which the deviation from Arrhenius' law will be unnoticeable:

$$(\delta T)_a \leqslant \frac{2\delta E_{eff}}{|\Delta E|}\,\frac{(\Delta T)^2}{T}, \qquad (a')$$

$$(\delta T)_b \leqslant \frac{2\delta E_{eff}}{E_{eff} - E}\,\Delta T. \qquad (b')$$

Assuming δE_{eff} = 10 kcal/mole, ΔE = 25 kcal/mole, E = 20 kcal/mole, T = 500°, ΔT = 200° we get:

$$(\delta T)_a \leqslant 60°$$

or

$$(\delta T)_b \leqslant 80°.$$

In Table 1 it can be seen that the measurements discussed were carried out in a range of 50°. This indicates that the assumption of an activation energy changing with increasing temperature along a curve of the type given in Fig. 2 is not inconsistent with the fact that simultaneously Arrhenius' law is found to be observed in the range of the measurements. A direct confirmation of the hypothesis would require a much greater temperature range, but as yet this is impossible because of experimental difficulties (the reaction time would increase to 10^2-10^3 hr).

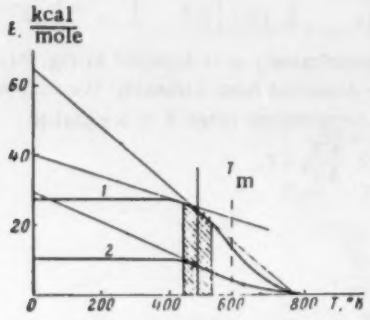

Fig. 2. Supposed relation between the activation energy of radical recombination in teflon and the temperature. 1) crystalline phase, 2) amorphous phase; the recombination is observed in the hatched temperature range.

We also remark that the assumption of a lowered activation energy at increasing temperature not only explains the high values of the measured (effective) activation energy and pre-exponential factor, but also gives quantitatively the compensation effect found in the experiments. In fact, now it can be taken for granted that for the various teflon samples (and analogously for the various hydrocarbon polymers) the actual vales of k^0 and E are nearly the same and that the variation in k^0_{eff} and E_{eff} is explained by different E(T) tions (1) and (2). Since in the temperature range in which the measurements are carried out the effective constant must approximately coincide with the actual value, it follows that:

$$\log k^0_{eff} - \frac{E_{eff}}{2.3\,RT} \simeq \log k,$$

so that

$$\log k^0_{eff} = \log k + \frac{E_{eff}}{2.3\,RT}$$

that is

$$\lg k^0_{eff} \simeq A + BE_{eff}. \qquad (4)$$

So, the slope of the straight lines depicted in Fig. 1 must be equal to $B=(2.3\,RT)^{-1}$ where T represents the mean temperature of the measurements. From the latter relation we obtained B = 0.47 mole/kcal for teflon, 0.655 for hydrocarbon polymers and the slopes of the straight lines in Fig. 1 are equal to 0.42 and 0.65 mole/kcal respectively. It is obvious that in this interpretation of the compensation effect relation (4) in principle, can only be approximately true, as is found in the experiment too. Thus, the compensation effect appears to be a consequence of the fact that in the experiment not the actual but the effective values of k^0 and E are measured. So we do not need to assume that there exists a relation between the actual pre-exponential factor and the activation energy, which assumption always gives great fundamental difficulties [12].

In conclusion we remark that the explanation given above for the compensation effect and the abnormal values of k^0 does not necessarily require the assumption that the phase changes at increasing temperature. The change in activation energy may also be connected with any other property inherent to the solid state. Therefore, the results obtained above may prove to be applicable not only to free radical recombinations in irradiated polymers but also to other reactions in the solid state for which a compensation effect and abnormal pre-exponential factors are found. Consequently, the main problem in theory is to substantiate and detect the shape of the relation between activation energy and temperature in those cases where the said energy is determined by crystal structure properties and not by the properties of the single reacting particles.

CONCLUSIONS

1. Experimental data on the reaction rate constants of radical recombinations in irradiated polymers have been discussed. A linear relation between $\lg k^0$ and E (compensation effect) and abnormally high pre-exponential factors has been found, which cannot be explained by existing theories.

2. Starting from various physical considerations it has been proposed that the activation energy is lowered at increasing temperatures (at temperatures close to the melting point of the polymer). It has been shown that this assumption enables us to explain the abnormally high pre-exponential factors as well as the occurrence of a compensation effect. It has been shown at the same time that in the temperature range in which the measurements are carried out the deviation from Arrhenius' law may be smaller than the inaccuracy of the measurements and, therefore, may not be noticed in the experiment.

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THE THEORY OF RADICAL REACTIVITY

1. A NEW INTERPRETATION OF THE POLAR EFFECT DURING COPOLYMERIZATION

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The activation energy of radical reactions may be represented as the sum of two terms. The first term is a linear function of the localization energies for the reacting molecules, the second term characterizes the polar effect and is expressed in the form $(x_1-x_2)^2$, where x_1 and x_2 are the acceptor-donor increments of the substituents in the reacting molecules. Copolymerization data and the Alfrey and Price equation are considered from this aspect.

The basic concepts of the theory of the influence of molecular structure on the rate of radical reactions (theory of radical reactivity)* were formulated about 12 years ago [1-4]. In the absence of steric hindrances the activation energy for a given series of reactions of the same type is determined by two factors: the conjugation effect and the polar effect. As was emphasized in the author's publications, when both the reacting molecules are hydrocarbons the second factor is inoperative and in some cases the theory leads to quantitative relationships between the activation energy (or the velocity constant) and values calculable by methods of quantum chemistry [4]. At present there is no quantitative theory of radical reactivity taking into account the polar effect.

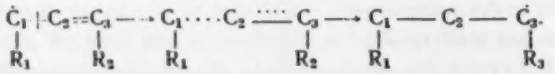
The great amount of experimental data accumulated on the velocity constants of copolymerization for many monomers with very different substituents at the double bond suggests the use of this material for checking theoretical conceptions of radical reactivity. For this reason, Alfrey and Price's equation [5], relating the copolymerization velocity constant to the "total" reactivity of a monomer Q and the polar factor e is of interest.

Although Alfrey and Price's equation covers a great amount of experimental material it does not have a theoretical basis (see below) and must be considered as empirical.

In the present paper a new method is proposed for taking account of the conjugation and polar effects in radical reactions, which differs essentially from Price's theory and is a further development of the author's work in this field and Bartlett and Nozaki's idea [6] of acceptor-donor reaction in the transition state.

Derivation of the Equation for the Velocity Constant

We will first consider the addition reaction of a radical to a double bond in the case of hydrocarbons.



* In the author's works the term "reactivity" (chemical) is used to signify any value which can serve as a kinetic characteristic of the position of the molecules (radicals) in a given series of reactions of the same type.

The author has previously shown [7] that the energy of the system radical + monomer during the course of a reaction event can best be represented as the sum E_{CCC} of the reaction energy of three carbon atoms with three π-electrons – "the quasiallyl radical" – and the values $\Delta E_{R_1CCC} + \Delta E_{R_2CCC}$, representing the conjugation energy of the R_1 and R_2 groups with a quasiallyl radical. All the components of this sum vary during the course of a reaction event, as a result of the conversion of the system from the initial state via the transitional to the final state. Since E_{CCC} is always far greater than the sum $\Delta E_{R_1CCC} + \Delta E_{R_2CCC}$, it may be assumed that the energy of the quasiallyl radical E_{CCC} in the transitional state assumes a certain value, independent of the groups R_1 and R_2.

On the basis of the common properties of hydrocarbons with conjugate bonds, it may be assumed that, if R_1 and R_2 are hydrocarbon groups, the sum $\Delta E_{R_1CCC} + \Delta E_{R_2CCC}$ during the course of a reaction event varies regularly (increasing or decreasing) from $\Delta E_{R_1\dot{C}} + \Delta E_{R_2C=C}$ in the initial state to $\Delta E_{R_1C} + \Delta E_{R_2C}$ in the final ($\Delta E_{R_1\dot{C}}$, $\Delta E_{R_2\dot{C}}$ and $\Delta E_{R_1C=C}$ are the conjugation energies of the R_1 and R_2 groups with the unpaired electron and the double bond, ΔE_{R_1C} is the conjugation energy of an R_1 group with an alkyl group). In the above-mentioned work it was shown that under these conditions the following equation is obtained for the activation energy E:

$$E = A' + \alpha^{\neq} |(E_{R_1\dot{C}} - \Delta E_{R_1C}) - (\Delta E_{R_2\dot{C}} - \Delta E_{R_2C-C})|, \qquad (1)$$

where A' and $\alpha^{\neq}$ are constants for a given series of reactions of the same type, $\alpha^{\neq}$ being somewhere between 0 and 1. Since the term in square brackets of equation (1) is equal to that part of the thermal effect of the reaction dependent on the R_1 and R_2 groups, equation (1) expresses Polyani's law.

Further, from equation (1) it follows that monomers and radicals taking part in reaction (1) can be arranged in universal series of reactivity, the series for monomers and their corresponding radicals being antibatic [3].*

Equation (1) can be written in another form by introducing the localization energies of Velandou ΔE_1 and ΔE_2 for atoms 1 and 2 in the radical and monomer. By definition: $\Delta E_1 = \Delta E_{R_1\dot{C}}$ and $\Delta E_2 = (E_{R_2} + 2\beta_{CC} + \Delta E_{R_2C=C}) - (E_{R_2} + \Delta E_{R_2\dot{C}}) = 2\beta_{CC} + \Delta E_{R_2C=C} - \Delta E_{R_2\dot{C}}$, where E_{R_2} and $2\beta_{CC}$ are the energies of the π-electrons of the R_2 and the isolated double bond, expressed by the resonance integral β_{CC} Hence for the activation energy we obtain the following equation:

$$E = A + \alpha^{\neq}(\Delta E_1 + \Delta E_2), \qquad (2)$$

where A is a constant.

To verify this equation it is convenient to proceed from the activation energies to the velocity constants. This can be done if we assume that in a series of reactions of the same type there is a linear relation between the logarithm of the pre-exponential and the activation energy. Hence, for a certain fixed temperature we obtain

$$\lg k = C - b(\Delta E_1 + \Delta E_2), \qquad (3)$$

where C and b are constants.

Fig. 1 gives the relation between log $k_{60°}$ and $\Delta E_1 + \Delta E_2$ for reactions having the necessary data (Table 1). The localization energies were calculated by the molecular orbit method. For the ethyl radical, $\Delta E_1 = 0.27\ \beta$. When this value was calculated for the conjugation coefficient of the methyl group the value 0.0375 [7] was assumed.

The straight line in Fig. 1 satisfies the equation:

$$\lg k_{60°} = 11{,}62 - 3{,}87(\Delta E_1 + \Delta E_2). \qquad (4)$$

We will now examine the reaction between molecules containing heteroatoms in R_1 and R_2 groups. In this case, apart from the influence of these groups on the conjugation or localization energies, a particular energy effect must be expected in the transition state, due to the difference in the acceptor-donor properties of the R_1

* For the reaction $\dot{R}_1 + HR_2 \rightarrow R_1H + \dot{R}_2$, where R_1 and R_2 are hydrocarbon groups, an equation, similar to equation (1), was obtained, from which the reactivity series for HR_2 molecules and its antibatic series for R_2 radicals follows [3].

TABLE 1.

Velocity Constants at 60° for Addition Reactions of Radicals to a Double Bond and the Localization Energy for Reacting Molecules

Reaction	Localization energy in β units for		Velocity constants at 60°, liters/mole sec.
	radical	monomer	
$\dot{C}H_3 + CH_2{=}CH{-}CH{=}CH_2$	0,00	1,64	185000
$\dot{C}H_3 + CH_2{=}CH_2$	0,00	2,00	6800
$CH_3{-}\dot{C}H_2 + CH_2{=}CH_2$	0,27	2,00	1000
$Ph{-}\dot{C}H_2 + CH_2{=}CH{-}CH{=}CH_2$	0,72	1,64	240
$Ph{-}\dot{C}H_2 + CH_2{=}CH{-}Ph$	0,72	1,70	180
$CH_2{=}CH{-}\dot{C}H_2 + CH_2{=}CH{-}CH{=}CH_2$	0,83	1,64	105
$CH_2{=}CH{-}\dot{C}H_2 + CH_2{=}CH{-}Ph$	0,83	1,70	75

Note. For explanation of table, see [4].

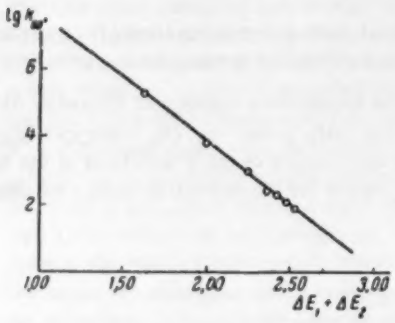


Fig. 1. Relation between the velocity constant at 60° of the addition reaction of a radical to a double bond, on the one hand, and the sum of the localization energies, on the other.

and R_2 groups. By analogy with the known fact of the strengthening of the bond in diatomic molecules A-B with different electronegativities of the A and B atoms (Pauling [8]) it may be considered that displacement of the electron cloud towards the more electron-acceptor group in the quasiallyl radical reduces the level of the transition state, i.e. reduces the activation energy. In the resonance method this strengthening of the bond is shown in an increase in the weight of the ionic structures of type A^+B^- or A^-B^+ in the case of diatomic molecules, or in an increase in the weight of ionic structures in the transition state during the reaction of a radical with the molecules [6]. Since the R_1 and R_2 groups are combined with the conjugation chain only in the transition state, the energy effect caused by the difference in the acceptor-donor properties of these groups is shown only in the transition state.

On the basis of this analogy with the properties of diatomic molecules, the energy effect in the transition state, caused by the difference in the acceptor-donor properties of the R_1 and R_2 groups, can be represented in the form proposed by Pauling for diatomic molecules: $(x_1 - x_2)^2$, where x_1 and x_2 are the acceptor-donor increments for the R_1 and R_2 groups. Thus, we arrive at the following general equation for the activation energy.

$$E = A + \alpha^{\mp} (\Delta E_1 + \Delta E_2) - (x_1 - x_2)^2 \qquad (5)$$

and the velocity constant

$$\lg k = C - b (\Delta E_1 + \Delta E_2) + (x_1 - x_2)^2. \qquad (6)$$

As may be seen from a comparison of equations (2) and (5), the acceptor-donor effect leads to a deviation from the Polyani Law in the direction of lesser values of the activation energies.

In principle, for molecules containing heteroatoms the localization energies may also be calculated theoretically (see, for example, [9]), but the values obtained in this way will depend on the selected values of the Coulomb and resonance integrals of the heteroatoms. To avoid the uncertainty associated with selection of

these values it is better to find the localization energies for different monomers and radicals from experimental data. The values of $\underline{x}$ should also be determined from experimental data.

Our proposed equation for the polar effect can be employed for other radical reactions. This problem will be examined in the next article. We will limit ourselves here to some general observations. For addition reactions of radicals to a phenyl ring (and other aromatic rings), equations (5) and (6) are retained, but with different values of the constants. For a reaction in which a hydrogen atom is split off

$$\begin{array}{l} \mathrm{C} \\ | \\ \mathrm{R} \end{array} + \mathrm{H} - \begin{array}{l} \mathrm{C} \\ | \\ \mathrm{R_2} \end{array} \rightarrow \begin{array}{l} \mathrm{C} \\ | \\ \mathrm{R_1} \end{array} \ldots \mathrm{H} \ldots \begin{array}{l} \mathrm{C} \\ | \\ \mathrm{R_2} \end{array} \rightarrow \begin{array}{l} \mathrm{C} \\ | \\ \mathrm{R_1} \end{array} - \mathrm{H} + \dot{\mathrm{C}} \begin{array}{l} | \\ \mathrm{R_2} \end{array}$$

an equation, similar to equation (1) [7], leads to the following expression for the activation energy

$$E = A_{\mathrm{H}} + \alpha_{\mathrm{H}}^{\neq} (\Delta E_1 - \Delta E_2) - a (x_1 - x_2)^2, \qquad (7)$$

where ΔE_1 and ΔE_2 are the localization energy of the electron in the initial and final radical, A_H, $\alpha^{\neq}$ and a are constants.

Copolymerization

To check equation (6) and find the above-mentioned values, it is first desirable to employ the numerous data on copolymerization velocity constants. The determination of the composition of a copolymer in relation to the composition of a mixture of monomers A and B makes it possible to find two values r and r_{BA}, which are associated with the velocity constants of four addition reactions of radicals to a double bond (chain-increase reactions)

$$\dot{\mathrm{A}} + \mathrm{A} \xrightarrow{k_{AA}} \dot{\mathrm{A}}, \qquad \dot{\mathrm{A}} + \mathrm{B} \xrightarrow{k_{AB}} \dot{\mathrm{B}},$$

$$\dot{\mathrm{B}} + \mathrm{A} \xrightarrow{k_{BA}} \dot{\mathrm{A}}, \qquad \dot{\mathrm{B}} + \mathrm{B} \xrightarrow{k_{BB}} \mathrm{B}$$

in the following manner:

$$r_{AB} = \frac{k_{AA}}{k_{AB}} \text{ and } r_{BA} = \frac{k_{BB}}{k_{BA}},$$

where the first letter in the index refers to the radical, and the second to the monomer. Employing equation (6) for the velocity constants we obtain the following equation for the constants r_{AB} and r_{BA}

$$\lg r_{AB} = -b (\Delta E_A - \Delta E_B) - (x_A - x_B)^2, \qquad (8)$$

$$\lg r_{BA} = -b (\Delta E_B - \Delta E_A) - (x_B - x_A)^2, \qquad (9)$$

where they indicate the localization energy of the monomers A and B and the acceptor-donor increments of the substituents in these monomers.

Adding and subtracting equations (8) and (9) we obtain:

$$\lg r_{AB} + \lg r_{BA} = -2 (x_A - x_B)^2, \qquad (10)$$

$$\lg r_{AB} - \lg r_{BA} = -2b (\Delta E_A - \Delta E_B). \qquad (11)$$

If equation (11) is written for monomers A and Z, and one equation is subtracted from the other, we obtain

$$\lg \frac{r_{BZ}}{r_{ZB}} = \lg \frac{r_{BA}}{r_{AB}} + \lg \frac{r_{AZ}}{r_{ZA}}. \qquad (12)$$

Equation (12) combines the copolymerization constants for three monomers. If monomers A and B are fixed and different Z monomers are taken, equation (12) will express a linear relation between $\log(r_{BZ}/r_{ZB})$ and $\log(r_{AZ}/r_{ZA})$. By fixing any other monomer instead of monomer B and varying the Z monomers we obtain a family of parallel straight lines with a tangent of the angle of slope of 1. This family of straight lines is shown in Fig. 2, styrene being taken as monomer A. The section intercepted by the straight line on the abscissa is equal to $-2b \times (\Delta E_A - \Delta E_B)$, hence ΔE_B can be determined because $b = 3.87$ [equation (4)] and ΔE_A for styrene is 1.704 β (theoretical value).

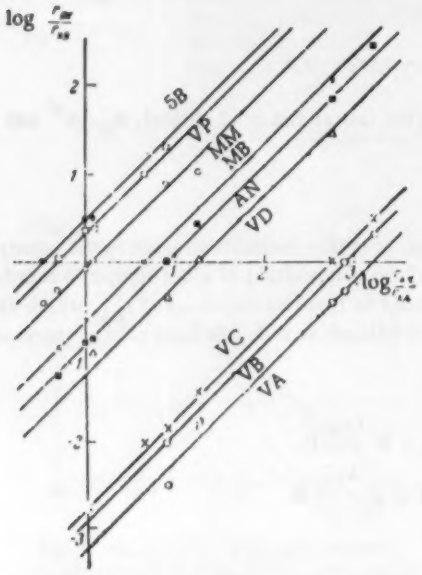


Fig. 2. Family of straight lines, plotted according to equation (12): B-butadiene; VP-2-vinyl pyridine; MM-methyl methacrylate; MA-methyl acrylate; AN-acrylonitrile; VD-vinylidene dichloride; VC-vinyl chloride; VB-vinyl benzoate; VA vinyl acetate.

The absolute value of the difference $|x_B - x_A|$ can be found from equation (10). In this difference we let the value of x for the group exhibiting the more electron-acceptor properties represent the minuend. It will subsequently be assumed that for styrene, or more accurately, for the phenyl group, $x = 0$.

If the values of E_A, x_A, ΔE_B and x_B are established fairly reliably for monomers A and B, the corresponding values for monomer Z are often better determined by combining equation (8) with the analogous equations for the pair of monomers A and Z or B and Z.

Table 2 gives the values found for the localization energies and the values of x.

The localization energies for polymeric radicals were calculated from the homopolymerization velocity constants according to equation (6), assuming $x_1 = x_2$.

The following values (liter/mole-sec) were assumed for the homopolymerization velocity constants at 60°: vinyl acetate 2040, methyl acrylate 1260, methyl methacrylate 575 (all these data are taken from [4]) and acrylonitrile 1000 (calculated from the data of [10] and [11].

Comparison with Price's Theory

It is easily shown that the equations (7) and (8) obtained by the author for r_{AB} and r_{BA} can be converted to Alfrey and Price's equations. The "total" reactivity of a monomer Q_A and the polarity factor e_A are combined with ΔE_A and x_A by the equations:

$$\lg Q_A = -b\,\Delta E_A + (x_A - K_1)^2 - K_2,$$
$$e_A = (2 \cdot 2{,}31)^{1/2}(x_A - K_1),$$

where K_1 and K_2 are constants. If we assume for styrene that $Q = 1.00$ and $e = -0.80$, then $K_1 = 0.372$ and $K_2 = 6.46$.

Equations (8) and (9) have a far sounder theoretical basis than Alfrey and Price's equation. In actual fact, in this equation the value of Q does not have a distinct physical sense, whereas the values of ΔE_1 and ΔE_2 of equations (2) and (5), from which equations (8) and (9) are derived, have a clear physical sense and can be calculated theoretically independently of kinetic measurements. As was pointed out, the value $(\Delta E_1 + \Delta E_2)$, expressed in corresponding units, represents the part of the thermal effect of a reaction, dependent on the substituents in the radical and at the double bond in a monomer.

TABLE 2.

Localization Energy and Acceptor-Donor Increments for Monomers and Polymeric Radicals

Monomer	Localization energy in β units for		Value of x for the corresponding substituent
	monomer	polymeric radical	
Butadiene	1.644	0.83	0.
2-Vinyl pyridine	1.663	–	0.25
Styrene	1.704	0.72	(0.0)
Methyl methacrylate	1.713	0.58	0.55
Methyl acrylate	1.788	0.42	0.68
Acrylonitrile	1.820	0.41	0.92
Vinylidene chloride	1.866	–	0.57
Vinyl chloride	2.058	–	0.34
Vinyl benzoate	2.076	–	0.25
Vinyl acetate	2.118	0.046	0.25

According to Price's theory [5, 12] the polar effect is caused by electrostatic reaction of the dipoles of a monomer and a radical in the transition state, the value of e characterizing the charges of these dipoles. Serious objections can be raised against this conception. A conclusion from this theory is that during the homopolymerization of weakly polar molecules of α-methyl styrene, isobutylene and styrene the electrostatic reaction has the same value as for strongly polar molecules of methacrylonitrile and acrylonitrile, because the absolute values of e for both these groups of monomers are almost equal and only differ as regards sign. It is also incomprehensible why e is the same for a monomer and its corresponding radical. These objections are equally valid if we assume that e characterizes the "polarizability" of the radicals and monomers, not the charges of constant dipoles.

The difficulties of Price's theory are eliminated in the interpretation of the polar effect presented in this paper, because the value x characterizes the acceptor-donor properties of groups attached to a quasiallyl radical in the transition state, not the charges of a monomer and a radical. Since it is assumed that the structure of the transition state is the same during the reaction of a radical A with a monomer B and a radical $\dot{B}$ with a monomer $\dot{A}$, it follows that the polar effect must be the same in both cases. Hence it also follows that the polar effect during homopolymerization is zero.

SUMMARY

Radical reactions in which hydrocarbons participate obey Polyani's Law. This makes it possible to represent the activation energy (or the logarithm of the velocity constant) of the addition of a radical to a double bond or an aromatic ring as a linear function of the sum of the localization energies for the radical and the molecule [equations (2) and (3)]. For reactions involving transfer of a hydrogen atom the activation energy is a linear function of the difference between the localization energies for the initial and final radicals.

If the reacting molecules contain heteroatoms it is necessary to take into account the acceptor-donor effect in the transition state, which it is proposed to express in the form $(x_1-x_2)^2$, where x_1 and x_2 are the acceptor-donor increments of the substituents in the radical and the molecule respectively. The acceptor-donor effect leads to a deviation from Polyani's Law towards smaller values of the activation energies [equations (5) (6) and (7)]. Equations (8) and (9) for the copolymerization constants r_{AB} and r_{BA}, expressed by the localization energies and the acceptor-donor increments, can be converted to the Alfrey and Price equations. At the same time, the proposed interpretation of the polar effect is free from the shortcomings of Price's theory.

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LIQUID-AND GAS-PHASE OXIDATION OF ETHYL ALCOHOL UNDER COMPARABLE CONDITIONS

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The kinetics of ethyl alcohol oxidation has been studied in the liquid and the gas phase under comparable conditions. It has been established that the mechanism changes when one switches from the liquid to the gas phase oxidation. It has been shown that the relatively high density in the liquid state is not the entire explanation of the difference found between the mechanism of the alcohol oxidation in the gas and the liquid phase.

Nowadays the oxidation of hydrocarbons and other organic compounds is of great importance as one of the routes for the direct synthesis of monomers and starting materials in the industrial production of polymers.

Until recently the oxidation of low-molecular organic substances was mainly carried out in the gas phase. The application of an idea proposed by one of us [1], namely, to change-over in these reactions to oxidation in liquid phase, proved to be far more promising. The high effectivity of the latter type of process was proved by using as an example the oxidation of liquefied n-butane under conditions close to the critical ones [2].

The differences in the kinetics and the reaction product composition, which are found when the state of aggregation of the substance to be oxidized is changed, puts forward the task of examining the oxidation mechanism in the gas and in the liquid phase under comparable conditions.

Hitherto this question has hardly been discussed in the literature. There exists the viewpoint expressed by N. N. Semenov that the course of the reaction in the gas phase is determined by competitive radical reactions, which are dependent upon the temperature and the pressure at which the oxidation is carried out [3].

As the object to be investigated in this study we have chosen ethyl alcohol, since its critical constants (temperature 243°, pressure 60 atm) allow examining the oxidation in the liquid phase in a rather broad range of temperatures and pressures.

The formation of a great number of reaction products containing, as a rule, less carbon atoms than the original substance is characteristic for the oxidation of alcohol in the gas phase [4]. So, methyl alcohol, methane, CO and other low-molecular products are formed in great amounts, when ethyl alcohol is oxidized at the temperature 295° and the pressure 150 mm Hg [5]. Here not more than 50% of the alcohol consumed is converted into valuable oxygen compounds.

The oxidation of ethyl alcohol in the liquid phase has been investigated at relatively low temperatures (below 100°) using various catalysts and reaction stimulators [6-9]. Papers on the oxidation of ethanol by the bound oxygen of $KMnO_4$ [10, 11], MnO_2 [12], $Ce(ClO_4)_4$ [13], CrO_3 [14, 15] and other compounds and by molecular oxygen under the action of ionizing radiations [16, 17], electric discharges [18], ultrasonic vibrations [19] are known.

Up to this time the oxidation of ethyl alcohol at temperatures and pressures close to the critical values has not been discussed in the literature. The latter range gives the most suited working conditions for tackling the problem of comparing the oxidation mechanism in the liquid and the gas phase.

Method of measuring. The oxidation of ethyl alcohol was carried out in the stainless steel autoclave arrangement which has been described in detail in the paper [2]. The reactor consisted of a cylindrical vessel provided with tubes for the thermocouple, the air to be bubbled through and the taking of samples. The alcohol evaporating from the reactor entered two reflux coolers (cooled with water and carbon dioxide) placed in series and in the form of condensate it was returned to the reactor. Samples of liquid and gaseous reaction products were taken at fixed time intervals after the start of the reaction. The total peroxide, acid, ester content and the amount of carbonyl compounds were determined by conventional chemical methods. The separate determination and identification of the individual carbonyl compounds and alcohols were done by means of a paper chromatography method which we have developed specially for the purpose of analyzing the oxidation products of low-molecular hydrocarbons and alcohols [20, 21].

Formic acid was determined (after neutral compounds had been distilled off with steam) by oxidizing it with potassium permanganate and acetic acid from the difference between the total acid content and the amount of formic acid as was determined in a separate sample.

Oxidation in the liquid phase

The oxidation of ethyl alcohol in the liquid phase was carried out at the temperatures 145-230° and the pressures 52-95 atm. Acetic acid and ethylacetate, the total amount of which corresponds to 80% of the ethyl alcohol consumed, are the main reaction products under these conditions. Kinetic curves for the consumption of ethyl alcohol and the accumulation of all reaction products at three temperatures (145, 200 and 230°) and pressure 52 atm are shown in Fig. 1.

At increasing temperatures the reaction rate is raised considerably. The activation energy calculated from the kinetic curves of ethyl alcohol consumption is equal to 10.2 kcal/mole. The numerical value of the ratio between the separate reaction products changes somewhat when the temperature is raised. So, the maximum acetic acid concentration in the reacting mixture increases from 10 mole% at 145° to 40 at 230° (Fig. 1, B). Formic acid is formed in small amounts (not more than 2%), but its yield relative to acetic acid increases when the temperature is raised. The esters formed in the oxidation of ethyl alcohol consist mainly of ethylacetate. The amount of formic acid esters does not exceed 3 mole% of the entire ester content, whereas this ratio does not change when the temperature is raised.

The yield of CO_2 is sharply raised at increased temperature (Fig. 1, E). In the same figure is shown the curve of CO accumulation (CO appears in very small amounts in the reaction products of the ethyl alcohol oxidation in liquid phase only at the temperature 230° and is absent at lower temperatures).

As intermediary products of ethanol oxidation in the liquid phase are found acetaldehyde (Fig. 1, D) and peroxides (among them H_2O_2, Fig. 1, F). The absolute amount of peroxide is very small, namely, 0.2 mole%. Obviously, here, just as in the oxidation of liquefied butane under similar conditions, the accelerating action of pressure and the metallic reactor walls upon peroxide decomposition makes its appearance.

Formaldehyde and methyl alcohol, which are characteristic products of the oxidation in the gas phase, are practically completely absent in the oxidation in the liquid phase.

Data on the amount of reaction products formed and unchanged alcohol allow totaling up the carbon balance for various oxidation times (see table). The good fit of the balance indicates that under the conditions of our experiments no other products than those analyzed are formed.

Increasing the pressure for the reaction in the liquid phase to 70-95 atm has practically no influence upon the rate and the product composition of ethyl alcohol oxidation. Only some lowering of the maximum ester concentration is noticed (Fig. 2).

The application of cobalt acetate as a catalyst for the ethyl alcohol oxidation in liquid phase gave no perceptible acceleration whatever of the reaction nor a change in the composition of the reaction product (Fig. 3).

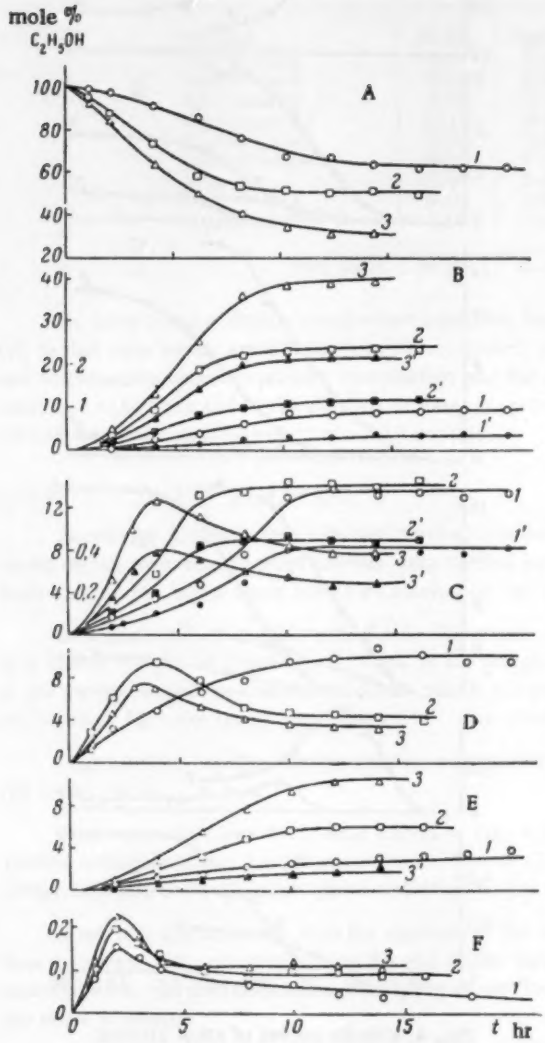


Fig. 1. Kinetic curves of ethyl alcohol consumption and reaction product accumulation in the oxidation at 52 atm and various temperatures: 1) 145°; 2) 200°; 3) 230°; A) ethyl alcohol consumption; B) acetic acid (without dash), formic acid (dash, right scale); C) ethylacetate (without dash), ethylformiate (dash, right scale); D) acetaldehyde; E) carbon dioxide (without dash), carbon monoxide (dash); F) peroxides.

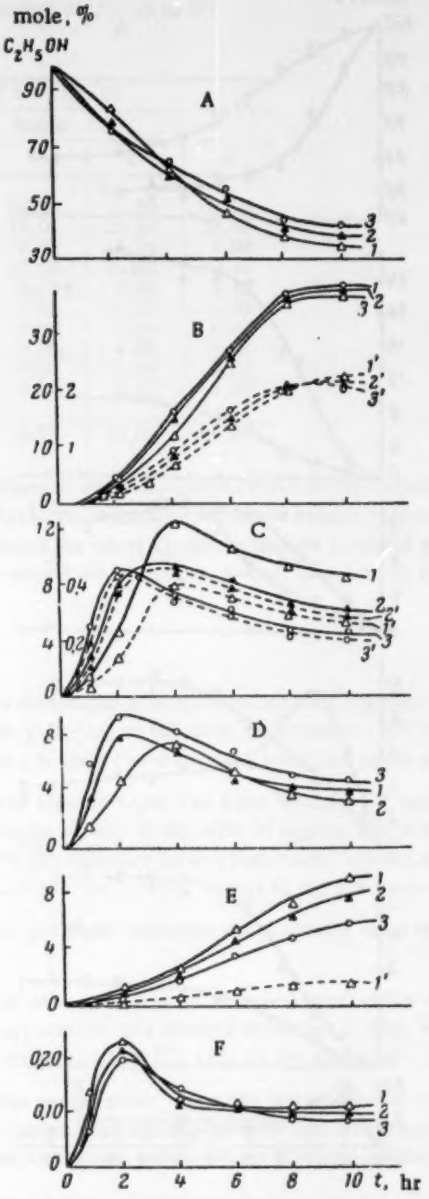


Fig. 2. Kinetic curves of ethyl alcohol consumption and reaction product accumulation for the oxidation in liquid phase at 230° and various pressures: 1) 52 atm; 2) 70 atm; 3) 95 atm. A) ethyl alcohol consumption; B) acetic acid (without dash), formic acid (dash, right scale); C) ethylacetate (without dash), ethylformiate (dash, right scale); D) acetaldehyde; E) carbon dioxide (without dash), carbon monoxide (dash); F) peroxides.

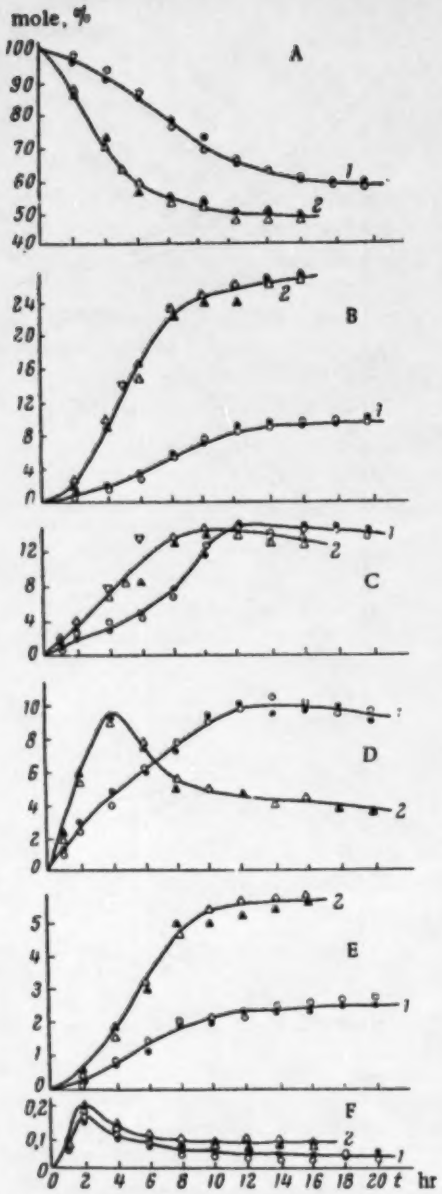


Fig. 3. Kinetic curves of ethyl alcohol consumption and reaction product accumulation for the oxidation in liquid phase at 52 atm and temperatures: 1) 145°; 2) 200°. The blackened marks indicate experiments in which 0.18 g cobalt acetate was added: A) ethyl alcohol consumption; B) acetic acid; C) ethylacetate; D) acetaldehyde; E) carbon dioxide; F) peroxides.

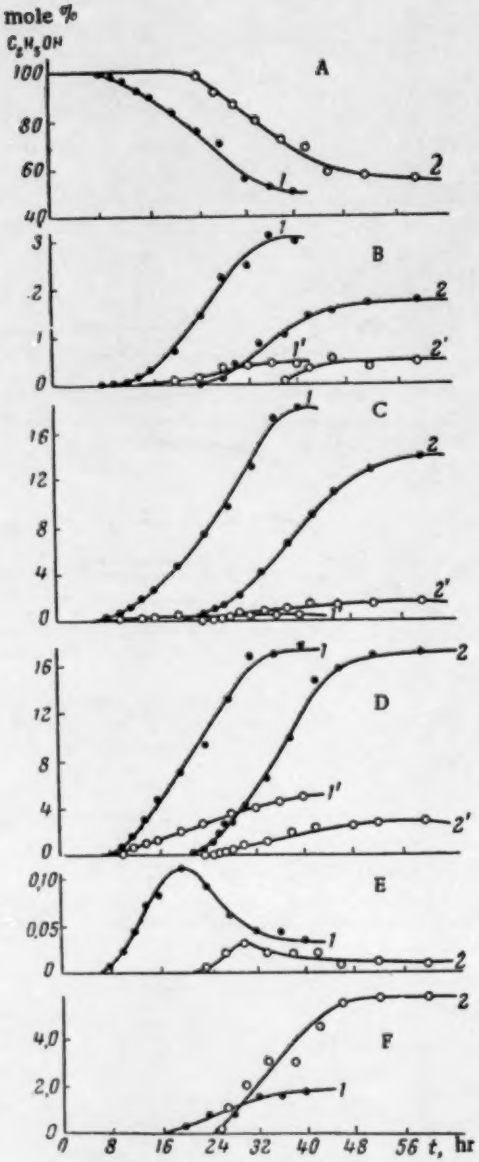


Fig. 4. Kinetic curves of ethyl alcohol consumption and reaction product accumulation for the oxidation in the gas phase (200°, 20 atm) at various initial concentrations of ethanol (mole/cm^3): 1) $2.6 \cdot 10^{-3}$; 2) $0.54 \cdot 10^{-3}$. A) ethanol consumption; B) acetic acid (without dash), formic acid (dash); C) acetaldehyde (without dash), formaldehyde (dash); D) carbon monoxide (without dash), carbon dioxide (dash); E) peroxides; F) methyl alcohol.

Balance of the reaction products for ethyl alcohol oxidation in the liquid phase at 200° and 52 atm.

Products	Mole % of ethanol fed				
	hours				
	2	4	6	8	10
Ethanol	87,00	72,50	55,40	52,80	51,00
Acetic acid	2,74	9,20	19,00	21,60	23,00
Formic acid	0,12	0,40	0,83	0,94	1,06
Ethylacetate	3,46	5,76	13,05	13,45	14,40
Ethylformiate	0,11	0,18	0,42	0,43	0,45
Acetaldehyde	6,00	9,60	7,80	5,00	4,50
Formaldehyde	0,00	0,00	0,00	0,00	0,00
CO_2	0,40	1,80	3,20	4,80	5,50
CO	0,00	0,00	0,00	0,00	0,00
Methanol	0,00	0,00	0,00	0,00	0,00
Sum total	99,83	99,44	99,70	99,02	99,91

We have found a similar result when oxidizing liquefied butane under conditions close to the critical ones [2]. In that case cobalt acetate practically completely annihilated the induction period for butane oxidation, but had no influence upon the product composition and the rate. Since the ethyl alcohol oxidation in liquid phase under our conditions and in the absence of catalysts proceeds without any induction period, it is natural that we did not find any catalytic effect of cobalt acetate.

Oxidation in the gas phase

In order to compare the oxidation mechanisms under the conditions of a different state of aggregation, experiments on the oxidation of ethyl alcohol were carried out in the gas phase at the same temperature (200°) as had been done in the liquid phase but at an alcohol partial pressure (20 atm) lower than the saturated vapor pressure.

In a first series of experiments the initial concentration of alcohol vapor was fixed at: $2.6 \cdot 10^{-3}$ mole/cm^3, in a second at $0.54 \cdot 10^{-3}$ mole/cm^3. Thus, in the gas phase without change in the state of aggregation a variation of the alcohol concentration was effected which was similar to the variation (about five times) occurring when we switched from the liquid phase oxidation (concentration $1.26 \cdot 10^{-2}$ mole/cm^3) to that in the gas phase.

The reaction kinetics and the product composition of the gas phase oxidation differ sharply from those in the liquid phase.

When one examines the kinetic curves of Fig. 4, in which data on both series of experiments of the ethyl alcohol oxidation in the gas phase are given, first of all, the appearance of a notable induction period, which is completely absent in the liquid phase oxidation at the same temperature (200°), attracts the attention.

Here it is characteristic that the duration of the induction period grows when the initial alcohol concentration is lowered. The reaction rate at the end of the induction period does not depend upon the initial alcohol concentration, but decreases considerably (by about five times), when one switches from the liquid phase to the gas phase oxidation.

The change in the state of aggregation has a still greater effect upon the composition of the reaction product.

So, instead of acetic acid and ethylacetate, acetaldehyde and CO are the main reaction products. Moreover, formaldehyde and methyl alcohol, which (just as CO) are completely absent in the liquid phase oxidation, make their appearance.

At the same time the variation in the initial alcohol concentration at the oxidation in the gas phase does not result in any substantial change in the composition and the amount of the products formed (Fig. 4).

The influence of temperature upon the ethanol oxidation in the gas phase was studied at the temperatures 200-280°, pressure 20 atm and the initial C_2H_5OH concentration of $2.6 \cdot 10^{-3}$ mole/cm^3 (Fig. 5). An increase in temperature results in a lower amount of acetic acid, acetaldehyde and peroxide formed and raised yields of

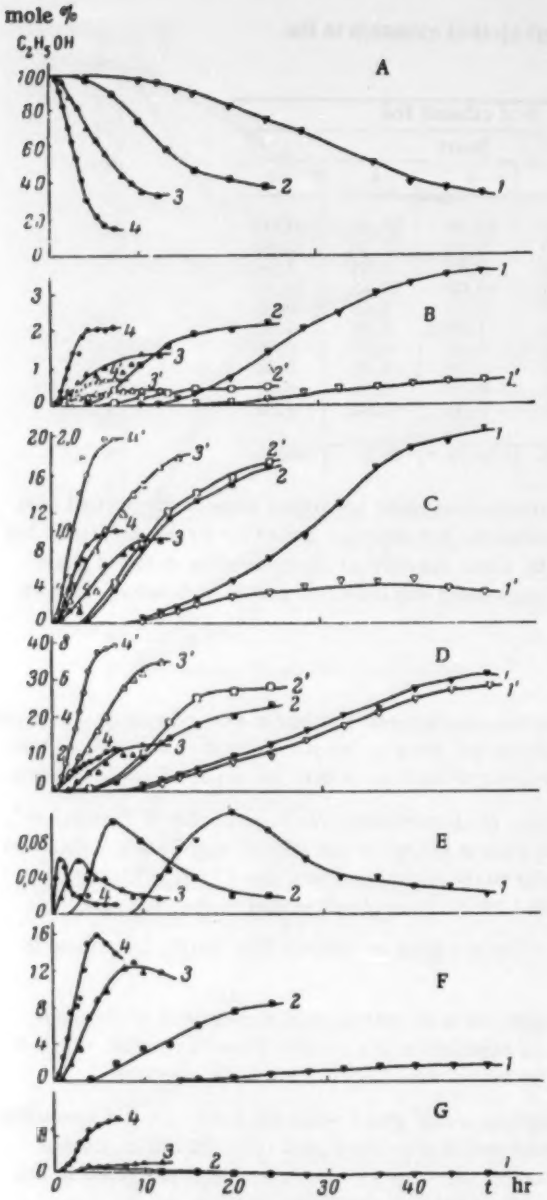


Fig. 5. Kinetic curves of ethyl alcohol consumption and reaction product accumulation for the oxidation in the gas phase (20 atm) at various temperatures: 1) 200°; 2) 230°; 3) 250°; 4) 280°. Initial alcohol concentration was $2.6 \cdot 10^{-3}$ mole/cm^3: A) ethanol consumption; B) acetic acid (without dash) and formic acid (dash); C) acetaldehyde (without dash) and formaldehyde (dash, right scale); D) carbon dioxide (without dash, right scale), carbon monoxide (dash); E) peroxides; F) methanol; G) methane.

formaldehyde, methyl alcohol, CO and methane. Raising the temperature has a particularly strong effect on the amounts of CO and CH_4.

Thus at increasing temperature the composition of the reaction end product is changed considerably in the direction of preferentially forming substances containing one carbon atom. The kinetic curves of alcohol consumption (Fig. 5, A) characterize the over-all reaction rate and enable us to calculate the activation energy, which is found to be 18 kcal/mole. A comparison of this value with the activation energy for oxidation in liquid phase (1.02 kcal/mole) points out that the mechanisms of the alcohol oxidation are different in the gas and in the liquid phase The difference in the mechanisms is still more evident from the change found in the product composition when one switches from the ethyl alcohol oxidation in the liquid phase to that in the gas phase.

At first sight the change in reaction course is in agreement with the competitive radical reactions proposed by Semenov. According to Semenov, in the course of a slow branched-chain oxidation the radical $RO_2^{\cdot}$ may react in two ways: it may either interact in a bimolecular reaction with the substance to be oxidized or isomerize and then decay monomolecularly.

When the oxidation is carried out at a constant temperature, the ratio between these two reaction directions for the radical $RO_2^{\cdot}$ is determined by the pressure, that is, by the concentration of the substance fed. On account of this, it may be supposed that in the liquid phase oxidation the bimolecular way of converting the radical $RO_2^{\cdot}$ will prevail.

In analogy to the oxidation mechanism of hydrocarbons, the main reactions proceeding at the ethyl alcohol oxidation in the liquid phase may be presented in the following way:

$$CH_3CH_2OH + O_2 \rightarrow CH_3\dot{C}HOH + HO_2^{\cdot};$$

$$CH_3\dot{C}HOH + O_2 \rightarrow CH_3CH(O-\dot{O})OH;$$

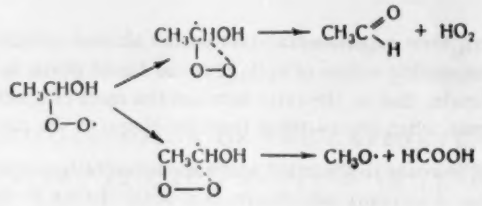
$$CH_3CH(O-\dot{O})OH + CH_3CH_2OH \rightarrow CH_3CH(OOH)OH + CH_3\dot{C}HOH;$$

$$CH_3CH(OOH)OH \rightarrow CH_3COH + H_2O_2;$$

$$CH_3COH \xrightarrow{O_2} CH_3COOH.$$

In this case acetic acid will be the main reaction product, which is also confirmed by the experimental results obtained in this study.

When one switches to the oxidation in the gas phase at the same temperature, the density of the reacting mixture increases and the monomolecular decay of the peroxide radical becomes more probable. The isomerization of the $RO_2^{\cdot}$ radical may proceed in two ways:



resulting in the formation of acetaldehyde and formic acid. Just as the former scheme was in the case of oxidation in the liquid phase, this latter is in agreement with the experimental data, since under the conditions of our experiments formic acid decomposes thermally into H_2O and CO and the latter substance is one of the main reaction products.

Under these conditions the second main product of the alcohol oxidation in the gas phase, acetaldehyde, is not oxidized further into acetic acid, obviously, because of the inhibiting action of C_2H_5OH, which is characteristic for the oxidation in the gas phase.

However, the change in the ethyl alcohol density cannot give the entire explanation of the difference found between the oxidation mechanism in the gas and in the liquid phase.

By starting from the above-stated theory of Semenov the ratio of the $RO_2^{\cdot}$ radical reactions in the gas phase can be compared with that in the liquid phase; this comparison indicates that such a small change (by about five times) in the density of the substance to oxidized, as is used in our experiments upon switching (at constant temperature) from liquid- to gas-phase oxidation, certainly will not result in such a sharp change in the course of the reaction.

In fact, we derive from the equations for the reaction rates of $RO_2^{\cdot} \xrightarrow{k_1} R'O + R''OH$ and $RO_2^{\cdot} + ROH \xrightarrow{k_2} RO_2H +$ $+ RO$ that $W_1 = k_1[RO_2^{\cdot}]$ and $W_2 = k_2[RO_2^{\cdot}][ROH]$. Consequently, at one and the same temperaure the ratio of these values should change proportionally to the concentration of the alcohol to be oxidized, that is, in our case the ratio W_2/W_1 for the oxidation in the liquid phase should be five times greater than that for the gas phase.

In order to estimate the value of k_2/k_1 from the experimental data we introduce the conception of the specific product fraction along each of the two reaction directions:

1) for the decay of the peroxide radical $\alpha_1 = \frac{W_1}{W_{form}}$;

2) for the interaction of $RO_2^{\cdot}$ with alcohol $\alpha_2 = \frac{W_2}{W_{form.}}$;

where $W_{form.} = W_1 + W_2$ is equal to the sum of the rates in which the products, which are characteristic for the oxidation in the gas and the liquid phase, are formed. In other words, W_1 is the formation rate of acetaldehyde, CO, methanol and other compounds which are the main products of the oxidation in the gas phase and W_2 represents the formation rate of acetic acid and ethylacetate. From the condition of stationary radical concentration we find the relation between α_1 and α_2 and the ratio k_2/k_1.

$$\frac{d[RO_2^{\cdot}]}{dt} = W_{form} - k_1[RO_2^{\cdot}] - k_2[RO_2^{\cdot}][ROH] = 0. \qquad (I)$$

When substituting the value of $[RO_2]$ given by relation (I) into the equations for W_1 and W_2 we get

$$W_1 = \frac{W_{form}}{1 + \frac{k_2}{k_1}[ROH]}; \quad W_2 = \frac{W_{form}[ROH]}{\frac{k_1}{k_2} + [ROH]}$$

or

$$\alpha_1 = \frac{1}{1 + \frac{k_2}{k_1}[ROH]}; \quad \alpha_2 = \frac{[ROH]}{\frac{k_1}{k_2} + [ROH]}.$$

As we know the values of α_1 and α_2 from experimental data on the alcohol oxidation in the liquid and the gas phase, we will calculate the corresponding values of k_2/k_1. For the liquid phase $k_2/k_1 = 1.7 \cdot 10^{-2}$ liter/mole, for the gas phase it is $2.2 \cdot 10^{-5}$ liter/mole, that is, the ratio between the rates of reaction (1) and (2) does not decrease by five times but by about 10^3 times, when one switches from the liquid to the gas.

At the same time a fivefold increase in the ethyl alcohol concentration at the oxidation in the gas phase (no change in the aggregation state of alcohol) only results in a small change in the values of α_1 and α_2, which is in agreement with the assumption of competitive radical reactions.

So, the conclusion may be drawn that not the relatively high density, which is characteristic for the liquid phase, but specific properties of the liquid substance are the main factors determining the rate and the course of the ethyl alcohol oxidation in the liquid phase. These specific properties may be, for instance, the influence of intermolecular hydrogen bonds or the occurrence reactions via ions which are absent in the gas phase.

SUMMARY

1. We have investigated the kinetics of ethyl alcohol consumption and the accumulation of all reaction products during the oxidation in the liquid and the gas phase at various temperatures and pressures.

2. It has been established that the reaction mechanism changes when one switches from liquid- to gas-phase oxidation. This finds its expression in a changed activation energy (10.2 kcal/mole for the liquid phase and 18.0 kcal/mole for the gas phase) and in a sharply changed composition of the oxidation product.

3. The results obtained have been discussed by starting from the assumption that the peroxide radical takes part in competitive reactions and it has been proved that the high density, which is characteristic for the liquid state, does not explain entirely the difference found between the mechanisms of ethyl alcohol oxidation in the gas and the liquid phase.

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THE KINETICS OF THE ACTIVATION OF THE CARBOXYL GROUP OF CARBOBENZOXYGLYCINE BY CYCLOHEXYL-β-[N-(N-METHYL-MORPHOLINIUM)]-ETHYLCARBODIIMIDE p-TOLUENE-SULFONATE

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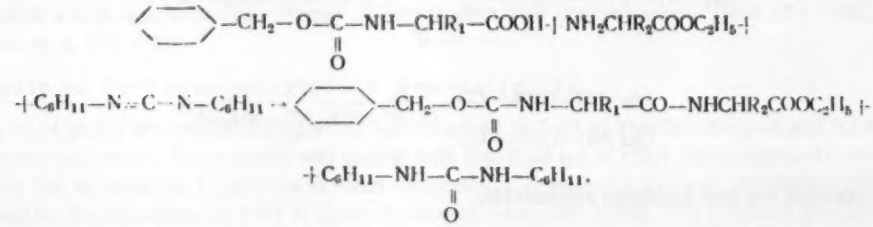
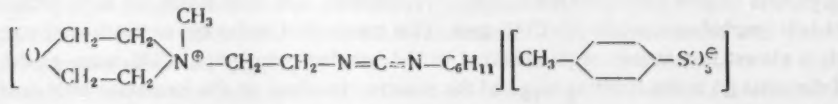
A study has been made of the reaction of cyclohexyl-β-[N-(N-methylmorpholinium)]-ethylcarbobenzoxyglycine, whose rate is determined by the rate of activation of the carboxyl group of the carbobenzoxyglycine. It has been shown that the reaction is accompanied by parallel acid-catalyzed hydrationof the carbodiimide. The rate constant for the activation of the carboxyl group of carbobenzoxyglycine in 50% dioxane has been found to be $3.9 \cdot 10^6 \exp(-10500/RT)$ liter/mole·sec and the activation energy of the acid-catalyzed hydration of the carbodiimide has been found to be 10.7 kcal/mole.

Disubstituted carbodiimides, particularly dicyclohexylcarbodiimide, have been extensively used in recent years for the synthesis of peptide and internucleotide bonds. The formation of a peptide bond proceeds in good yield when dicyclohexylcarbodiimide is added to a mixture containing a carbobenzoxy aminoacid and an aminoacid ester



In addition to cyclohexylcarbodiimide, which is insoluble in water, a number of water-soluble carbodiimides have been synthesized [1]. Solubility in water is ensured if one of the substituents contains a tertiary amino group or a quaternary ammonium group. A particular example of such a compound is cyclohexyl-β-[N-(N-methylmorpholinium)]-ethylcarbodiimide p-toluenesulfonate



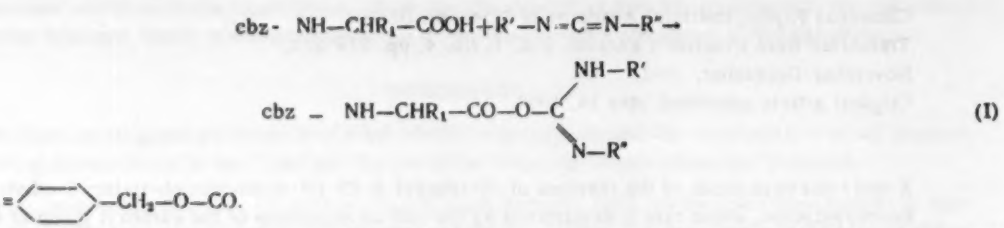
which is studied in the present work. For the sake of brevity we shall subsequently refer to this compound as CME carbodiimide.

Water-soluble carbodiimides can be used to carry out the synthesis of peptides in aqueous or water-containing solutions at room temperature in a near-neutral medium [1-3]. The synthesis of peptides by means of water-soluble carbodiimides thus provides a good model for studying the kinetics of the formation of peptide bonds under near-biological conditions.

All methods of peptide synthesis, including the synthesis of peptide bonds in the organism, are based on the preliminary conversion of the aminoacids to various aminoacyl derivatives (anhydrides, esters, azides) with a high acylating activity.

In biochemistry such derivatives have been called activated aminoacids. A characteristic property of activated aminoacids is the ability to react with hydroxylamine to give hydroxamic acids. The latter can readily be detected and determined quantitatively, since they form red complexes with Fe^{3+} ions.

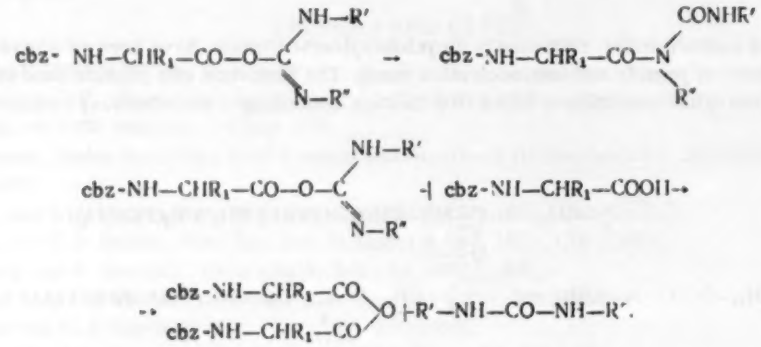
By analogy it may be assumed that the role of carbodiimides in peptide synthesis involves the activation of the carboxyl group of the aminoacids by the formation of an aminoacid ester with the enolic form corresponding to disubstituted urea [4, 5]



(I)

where cbz =

This hypothetical ester may subsequently react with the amino group of the aminoacid to give the dipeptide and R'R"-urea. In the absence of an amine, R'R"-carbodiimides react with acids to give either aminoacid anhydrides or N-aminoacyl-R'R"-urea. It is suggested that these products are formed from the same intermediate ester (I), which either isomerizes to N-aminoacyl-R'R"-urea or reacts with another aminoacid molecule to give the aminoacid anhydride and R'R"-urea:



Both products are also activated aminoacids.

The aim of the present work was to study the kinetics of the activation of carbobenzoxyglycine by means of CME-carbodiimide. Since carbobenzoxyglycine is sparingly soluble in water, the reaction was carried out in 1:1 by volume aqueous dioxane solutions.

The first experiments showed, however, that the reaction between carbobenzoxyglycine and CME-carbodiimide yields a product which reacts with hydroxylamine to give a hydroxamic acid but which does not react with ethyl glycinate to give ethyl carbobenzoxyglycylglycinate. The data which we have obtained suggest that this product is N-(carbobenzoxyglycyl)-CME-urea. This means that under our experimental conditions the intermediate ester (I) is almost instantaneously isomerized to N-(carbobenzoxyglycyl)-CME-urea. At the same time the formation of the ester (I) is the limiting stage of the reaction involved in the formation of N-(carbobenzoxyglycyl)-CME-urea, so that by measuring the rate of the latter reaction it is possible to measure the rate of activation of the carboxyl group of carbobenzoxyglycine by CME-carbodiimide.

EXPERIMENTAL

The Synthesis of Cyclohexyl-β-[N-(N-methylmorpholinium)]-ethylcarbodiimide p-Toluenesulfonate

A. The Preparation of N-(β-Aminoethyl)-morpholine. 95.6 g (0.67 mole) of β,β'-dichlorodiethyl ether (chlorex)was added over a period of one hour to 240 g (4 mole) of anhydrous ethylenediamine at the boil. The solution was boiled for a further half-hour, cooled, and 80 g (1.4 mole) of KOH was added. The precipitate of KCl was filtered off, washed with ethylenediamine, and the solution and wash liquid were dried for 10-12 hours over KOH. The lower layer (aqueous KOH solution) was then separated, the ethylenediamine was distilled from the upper layer, and the residue was fractionated. The yield of the fraction boiling at 196-208° was 51 ml (58% of the theoretical); n_{25} 1.4742; equivalent weight found by titration with 0.1 N HCl 65.6 (theoretical 65.0).

B. The Preparation of Cyclohexyl Isothiocyanate [7]. 50 ml (0.43 mole) of cyclohexylamine was dissolved in 400 ml of ether in a flask fitted with stirrer and reflux condenser and cooled with ice. 13 ml of CS_2 (0.22 mole) was then added dropwise. The ether was distilled off and the residue of cyclohexylammonium cyclohexyldithiocarbamate was treated with a hot solution of 56.5 g (0.21 mole) of $HgCl_2$ in 200 ml of water. The reflux condenser was replaced by a straight condenser and the mixture was boiled. The cyclohexyl isothiocyanate distilled in the steam as it was formed. It was then extracted with ether, dried over ignited Na_2SO_4, the ether was distilled off, and the product redistilled. The fraction boiling at 219° was collected. The yield of cyclohexyl isothiocyanate was 20 g (66% of the theoretical) (literature data: b.p. 219°).

C. The Preparation of β-(N-Morpholinyl)-ethylcyclohexylthiourea [1]. 11.6 g (0.08 mole) of cyclohexyl isothiocyanate was dissolved in 250 ml of ether and 10.7 g (0.08 mole) of N-(β-aminoethyl)-morpholine was added. The solution was boiled for 10 minutes and left overnight. 20.4 g (91.5% of the theoretical) of β-(N-morpholinyl)-ethylcyclohexylthiourea crystallized. B.p. 125° (literature data: m.p. 128°).

D. The Preparation of β-(N-Morpholinyl)-ethylcyclohexylcarbodiimide (the Base). 4.0 g (0.015 mole) of β-(N-morpholinyl)-ethylcyclohexylthiourea was heated with 6.0 g (0.03 mole) of freshly precipitated yellow mercuric oxide in 50 ml of acetone for one and a half hours. (The mercuric oxide was precipitated from 10% $HgCl_2$ solution with the stoichiometric quantity of 1.5 N NaOH at room temperature. The precipitate was filtered off and washed on the filter with water, methyl alcohol and ether, and dried at 37°). The HgS precipitate was filtered off, the acetone solution was evaporated in vacuo, the residual oil was dried by three-fold distillation with absolute benzene, and redistilled in vacuo at 2 mm Hg pressure. The fraction boiling at 167° was collected. The yield of the carbodiimide base was 2.4 g (70% of the theoretical).

E. The Preparation of Cyclohexyl-β-[N-(N-methylmorpholinium)]-ethylcarbodiimide p-Toluenesulfonate (the Carbodiimide Salt). 10 g (0.04 mole) of the carbodiimide base and 7.8 g (0.04 mole) of methyl p-toluenesulfonate were heated for 20 minutes on a water bath at 90°. The mixture was cooled and the resultant oil was treated with absolute ether.

The crystals which separated were filtered off and washed with absolute ether. Yield 13 g (74%). M.p. 114° (literature data: m.p. 113-115°).

The Synthesis of Carbobenzoxyglycine Anhydride [8]

0.418 g (2.14 mole) of carbobenzoxyglycine was dissolved in 2 ml of absolute dioxane and 0.24 g of absolute triethylamine was added. The solution was cooled with ice, 0.19 ml of ethyl chlorocarbonate was added, and the mixture was left to stand for 10 minutes at room temperature. A further 0.418 g of carbobenzoxyglycine and 0.24 ml of absolute triethylamine in 2 ml of absolute dioxane were then added. The resultant precipitate of carbobenzoxyglycine anhydride was filtered off and washed with absolute dioxane and absolute alcohol. Yield 0.65 g (81% of the theoretical). M.p. 120° (literature data: m.p. 119°.

The activated carbobenzoxyglycine was determined by the hydroxamate reaction [9]. A mixture of 4 ml of 0.4 N hydroxylamine sulfate and 2 ml of 1.0 N NaOH, previously cooled to 0°, was added to 2 ml of the specimen to be analyzed. After 2 minutes, 2 ml of 0.1 M $Fe_2(SO_4)_3$ in 2 N H_2SO_4 was added. The resultant colored solution was filtered and the optical density measured on an FÉK-M apparatus with green light filter and 20 mm cell. The optical density depends on the temperature at which the hydroxamate formation is carried out. This indicates that the conversion of the activated carbobenzoxyglycine to carbobenzoxyglycine hydroxamate is not quantitative; part of the original material is apparently hydrolyzed. In order to obtain reproducible results, therefore, it is necessary to carry out the preparation of the hydroxamates at a definite temperature and at a definite ratio of hydroxylamine to NaOH.

In the experiments on the study of the kinetics of hydration of CME-carbodiimide, the concentration of the latter was determined by adding 1 ml of 0.2 M carbobenzoxyglycine in 0.1 N NaOH in 50% aqueous CH_3OH to the test specimen and allowing the mixture to stand at room temperature. After 20 minutes the quantity of activated carbobenzoxyglycine formed was determined by the method described above.

EXPERIMENTAL RESULTS

The first experiments showed that some time after solutions of carbobenzoxyglycine in methyl alcohol, dioxane, or tetrahydrofuran and of CME-carbodiimide in water are mixed, the system gives a positive hydroxamate reaction, i.e. activation of the carboxyl group of the carbobenzoxyglycine takes place. The resultant activated carbobenzoxyglycine is stable in neutral and acid solution. In 50% dioxane in the presence of 0.0225 M $Na_2B_4O_7$ + 0.005 N H_2SO_4, hydrolysis of the activated carbobenzoxyglycine takes place; the rate constant for the reaction is 0.37 min^{-1} at 21°.

The stable products of the reaction of carbobenzoxyglycine with CME-carbodiimide, giving the hydroxamate reaction, may be either carbobenzoxyglycyl-CME-urea or carbobenzoxyglycine anhydride. In order to decide which of these two products was in fact formed, we studied the kinetics of hydrolysis of carbobenzoxyglycine anhydride in 50% dioxane. The hydrolysis proceeded very rapidly showing first order kinetics with a rate constant of 0.21 min^{-1} at 18°.

Since the compound formed in the reaction between carbobenzoxyglycine and CME-carbodiimide remains almost undecomposed for several hours, it cannot be carbobenzoxyglycine anhydride and is more likely to be carbobenzoxyglycyl-CME-urea. We shall subsequently refer to this compound as activated carbobenzoxyglycine.

Since in 50% methyl alcohol the reaction of carbobenzoxyglycine with CME-carbodiimide is too rapid (the reaction is almost complete in 2-3 minutes at 20°), the main kinetic studies were carried out in 50% dioxane, in which the reaction proceeds at a rate convenient for measurement.

Figure 1 gives the curve obtained by means of the hydroxamate reaction for the accumulation of activated carbobenzoxyglycine at initial concentrations of carbobenzoxyglycine and CME-carbodiimide of 0.005 M at a temperature of 50°. After 50 minutes the activated carbobenzoxyglycine concentration reaches a limiting value D_∞ and subsequently remains almost constant. In order to establish what fraction of the carbobenzoxyglycine is converted to activated carbobenzoxyglycine, values of D_∞ were obtained for different excess CME-carbodiimide concentrations at constant initial carbobenzoxyglycine concentration. Figure 2 gives the relationship obtained in this way between D_∞ and the initial CME-carbodiimide concentration $[CDI]_0$. It can be seen that D_∞ increases with increase in $[CDI]_0$ and reaches a constant value D_{max} at a three- to four-fold excess of CME-carbodiimide. The fact that there is no further increase in the yield of activated carbobenzoxyglycine gives grounds for assuming that when this excess is present, all the carbobenzoxyglycine is converted to its activated derivative. This assumption was subsequently used to determine the yield ζ of activated derivative (cbz-gly*) as a fraction of the carbobenzoxyglycine (cbz-gly) taken, i.e. it was assumed that

$$\zeta = \frac{[\text{cbz-gly*}]}{[\text{cbz-gly}]} = \frac{D}{D_{max}}.$$

Figure 3 gives the kinetic curve calculated in this way for the accumulation of activated carbobenzoxyglycine at 19.8° and initial carbobenzoxyglycine and CME-carbodiimide concentrations of 0.005 M. It can be seen that when the reagent ratio is stoichiometric, the reaction is only 51% complete. It can easily be shown that the low yield of activated carbobenzoxyglycine does not result from the attainment of thermodynamic equilibrium. In the first place, if the equilibrium concentration of the reaction product is 51% for a stoichiometric reagent ratio, the yield would be only 82% for a three-fold excess of one of the reagents. For a three-fold excess of CME-carbodiimide, however, the yield is close to 100%. Secondly, if thermodynamic equilibrium were established when the conversion were only half-completed, this would mean that the reverse reaction involving the decomposition of the activated derivative to carbobenzoxyglycine and CME-carbodiimide is rapid. Since CME-carbodiimide is extremely unstable in acid medium, then as a result of the rapid reverse reaction the resultant activated derivative should be rapidly and irreversibly decomposed in acid medium. Experiment shows, however, that the activated derivative of carbobenzoxyglycine is stable in acid medium.

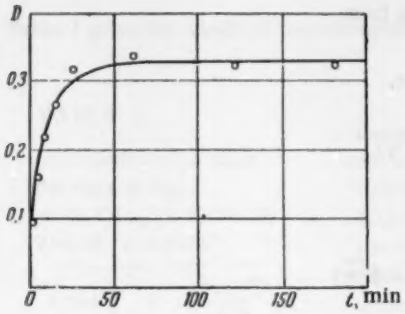


Fig. 1. Kinetics of the accumulation of activated carbobenzoxyglycine in the reaction of its 0.005 M solution with 0.005 M CME-carbodiimide in 50% dioxane at 50°.

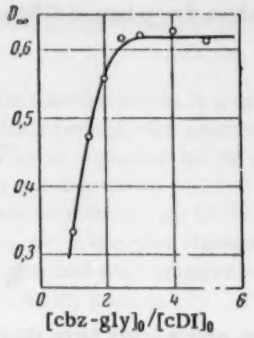


Fig. 2. Relationship between the limiting yield of activated carbobenzoxyglycine in M carbobenzoxyglycine solution in 50% dioxane at 50.0° on the ratio of the initial concentrations of CME-carbodiimide and carbobenzoxyglycine.

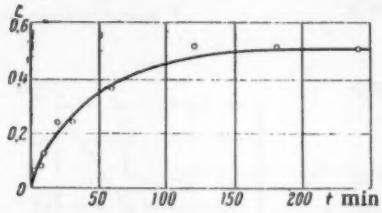


Fig. 3. Kinetic curve for the accumulation of activated carbobenzoxyglycine in the reaction of its 0.005 M solution with 0.005 M CME-carbodiimide in 50% dioxane at 19.8°. ζ is the dimensionless concentration of activated carbobenzoxyglycine (the curve is constructed from Eq. (4) with $\varkappa = 0.815$.

The low yield of activated carbobenzoxyglycine is thus apparently due to the fact that one of the reagents is used up in some other side-reaction. Since CME-carbodiimide is unstable in acid medium and undergoes acid-catalyzed hydration, the most probable suggestion is that the activation of carbobenzoxyglycine is accompanied by the acid-catalyzed hydration of CME-carbodiimide under the influence of the carbobenzoxyglycine behaving as an acid.

This assumption allows us to approach a quantitative description of the kinetics of the formation of the activated carbobenzoxyglycine. If we denote the CME-carbodiimide concentration by x, the carbobenzoxyglycine concentration by y, and the activated carbobenzoxyglycine concentration by z, we may write

$$\frac{dz}{dt} = k_1 xy,$$
$$-\frac{dx}{dt} = k_1 xy + k_0 [H^+]\, x, \qquad (1)$$

where k_1 is the rate constant of the bimolecular reaction involved in the formation of the activated carbobenzoxyglycine, and k_0 is the rate constant of the acid-catalyzed hydration of CME-carbodiimide.

Assuming that the degree of dissociation of carbobenzoxyglycine is small, we may write

$$[H^+] = \sqrt{Ky},$$

where K is the ionization constant of carbobenzoxyglycine. Introducing the dimensionless concentrations and parameters

$$\xi = \frac{x}{y_0}; \qquad \eta = \frac{y}{y_0}; \qquad \zeta = \frac{z}{y_0}; \qquad \varkappa = \frac{k_0\sqrt{K}}{k_1\sqrt{y_0}},$$

we can readily reduce the system of differential equations (1) to the form

$$-\frac{d\eta}{dt} = \frac{d\zeta}{dt} = k_1 y_0 \xi\eta,$$
$$-\frac{d\xi}{dt} = k_1 y_0 (\xi\eta + \varkappa\xi\sqrt{\eta}), \tag{2}$$

from which

$$\xi_0 - \xi = 1 - \eta + 2\varkappa(1 - \sqrt{\eta}).$$

In particular, over a fairly large time interval during which the CME-carbodiimide is almost completely used up, $\xi = 0$, $\eta = \eta_\infty$ and

$$\xi_0 = 1 - \eta_\infty + 2\varkappa(1 - \sqrt{\eta_\infty}).$$

This relationship enables us to find the parameter $\varkappa$ from the value ζ_∞ of the limiting yield of activated carbobenzoxyglycine obtained for a given ratio of initial concentrations of carbobenzoxyglycine and CME-carbodiimide. Thus if $\xi_0 = 1$,

$$\varkappa = \frac{1}{2} \cdot \frac{\zeta_\infty}{1 - \sqrt{1 - \zeta_\infty}}. \tag{3}$$

Expressing η and ξ in terms of ζ, we may write Eq. (2) in the form

$$\frac{d\zeta}{dt} = k_1 y_0 (1 - \zeta)[\xi_0 - \zeta - 2\varkappa(1 - \sqrt{1 - \zeta})].$$

The solution of this equation has the form:

at $(1 + \varkappa)^2 > \xi_0$

$$k_1 y_0 (1 + 2\varkappa - \xi_0) t = \ln\eta - \frac{\varkappa + \sqrt{(1+\varkappa)^2 - \xi_0}}{\sqrt{(1+\varkappa)^2 - \xi_0}} \ln \frac{\sqrt{\eta} + \varkappa - \sqrt{(1+\varkappa)^2 - \xi_0}}{1 + \varkappa - \sqrt{(1+\varkappa)^2 - \xi_0}} \tag{4}$$
$$+ \frac{\varkappa - \sqrt{(1+\varkappa)^2 - \xi_0}}{\sqrt{(1+\varkappa)^2 - \xi_0}} \ln \frac{\sqrt{\eta} + \varkappa + \sqrt{(1+\varkappa)^2 - \xi_0}}{1 + \varkappa + \sqrt{(1+\varkappa)^2 - \xi_0}};$$

when $(1 + \varkappa)^2 > \xi_0$, and

$$k_1 y_0 (1 + 2\varkappa - \xi_0) t = \ln\eta - \ln \frac{\eta + 2\varkappa\sqrt{\eta} + \xi_0 - 1 - 2\varkappa}{\xi_0} +$$
$$+ \frac{\varkappa}{\sqrt{\xi_0 + (1+\varkappa)^2}} \left[\operatorname{arctg} \frac{1 + \varkappa}{\sqrt{\xi_0 - (1+\varkappa)^2}} - \operatorname{arc\,tg} \frac{\varkappa + \sqrt{\eta}}{\sqrt{\xi_0 - (1+\varkappa)^2}} \right].$$

Thus having found the maximum yield of activated carbobenzoxyglycine ζ_∞, we can use formula (3) to calculate $\varkappa$. Knowing the value of ζ, and hence η, which is equal to $1-\zeta$, at a given moment of time t, i.e. having some point on the kinetic curve for the accumulation of activated carbobenzoxyglycine, we can determine the value of k_1. Knowing $\varkappa$ and k_1 we can calculate $k_0\sqrt{K}$.

Table 1 gives the results of the corresponding calculation for several points on the kinetic curve given in Fig. 3.

TABLE 1

Calculation of k_1 from the data in Fig. 3. ($t=19.8°$; $x_0=y_0=0.005$ M; $\zeta=0.51$; $\varkappa=0.815$)

t, min	c	k_1, liter·mole^{-1}·min^{-1}
3	0,065	4,80
6	0,079	2,92
10	0,126	3,12
20	0,236	3,56
30	0,243	2,52
60	0,366	2,72

$k_1=2.97\pm0.30$ liter·mole^{-1}·min^{-1}; $k_0\sqrt{K}=0.173$ liter$^{\frac{1}{2}}$·mole$^{-\frac{1}{2}}$·min^{-1}.

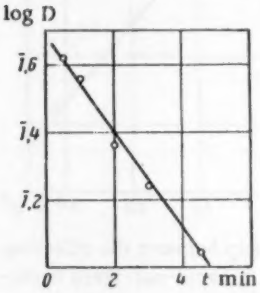


Fig. 4. The kinetic curve (on the semilogarithmic scale) for the hydration of CME-carbodiimide in 50% dioxane in the presence of 0.005 N HCl at 20°.

In order to determine the rate constant k_0 it is necessary to know the ionization constant of carbobenzoxyglycine under the conditions of our experiments. For this purpose we measured the pH of a solution of 0.005 M carbobenzoxyglycine in the presence of 0.005 M CME-carbodiimide by means of a glass microelectrode. An LP-57 potentiometer was used for the measurements. Since the glass electrode gives only relative pH values, the value obtained was compared with the value of the pH obtained for a 0.002 N HCl solution.

The results were reproducible only to within 0.05-0.1 pH unit, due to the instability of the surface of the glass electrode in the non-aqueous medium. Thus in one of the experiments the pH of 0.002 N HCl was found to be equal to 2.25 and the pH of the test solution 3.36. The hydrogen ion concentration in 0.005 M carbobenzoxyglycine solution in the presence of 0.005 M CME-carbodiimide is thus equal to $0.002 \times 10^{-1.11}=1.5 \cdot 10^{-4}$ M. The ionization constant of carbobenzoxyglycine at 20° is thus equal to

$$K=[H^+]^2/[cbz\text{-}gly]=4.5\cdot10^{-6}\ M,$$

from which

$$k_0=81\ \text{liter}\cdot\text{mole}^{-1}\cdot\text{min}^{-1}.$$

In order to verify the correctness of the assumption that the consumption of CME-carbodiimide is associated with the acid-catalyzed hydration of the carbodiimide, we also studied the kinetics of the acid-catalyzed hydration of CME-carbodiimide in the presence of HCl. Figure 4, with coordinates log D vs. time, gives the kinetic curve for the consumption of CME-carbodiimide at 20° in 50% dioxane in the presence of 0.005 N HCl. All the points lie on a straight line, i.e. the hydration of CME-carbodiimide is a second order reaction. The effective rate constant is equal to 0.332 min^{-1}, which gives the value $k_0=66.5$ liter·mole^{-1}·min^{-1} for the constant of the acid-catalyzed hydration; this value is close to that obtained from the data on the kinetics of the activation of carbobenzoxyglycine.

Table 2 gives the values of the rate constants k_1 and $k_0\sqrt{K}$ obtained at different temperatures and different ratios of carbobenzoxyglycine and CME-carbodiimide concentrations.

Figures 5 and 6 show how log k_1 and log $k_0\sqrt{K}$ depend on $1/T$. The points lie on a straight line within the limits of experimental error. From the slope of this line we find that $E_1=10.5$ kcal/mole and $E_2=10.7$ kcal/mole. The quantity E_2 is the sum of the activation energy of the acid-catalyzed hydration and half the heat of ionization of carbobenzoxyglycine in 50% dioxane.

The Arrhenius equation for the rate constant k_1 has the form

$$k_1=3.9\cdot10^6\,e^{-\frac{10500}{RT}}\ \text{liter}\cdot\text{mole}^{-1}\cdot\text{sec}^{-1}$$

SUMMARY

1. It has been shown that in 50% aqueous dioxane, tetrahydrofuran, or methyl alcohol, carbobenzoxyglycine reacts with cyclohexyl-β-[N-(N-methylmorpholinium)]-ethylcarbodiimide p-toluenesulfonate to yield a product which reacts with hydroxylamine to form a hydroxamate. The reaction is much more rapid in 50% methyl alcohol

TABLE 2

Values of the constants k_1 and $k_0\sqrt{K}$ at different temperatures

Temp., °C	Ratio of the initial concentrations of CME-carbodiimide and glycine, ξ_0	Limiting yield of activated glycine ζ_∞	k_1, liter · mole^{-1} · min^{-1}	$k_0\sqrt{K}$, liter$^{\frac{1}{2}}$ · mole$^{\frac{1}{2}}$ · min^{-1}
19,8	1,0	0,510	2,97±0,30	0,173
20,0	1,0	0,585	3,97±0,37	0,182
20,0	3,0	1,0	3,59±0,60	—
20,7	1,0	0,565	3,27±0,09	0,152
30,0	1,0	0,480	4,60±0,37	0,302
30,0	3,0	1,0	4,53±0,23	—
40,0	1,0	0,505	9,9±0,5	0,585
50,0	1,0	0,540	17,7±1,2	0,895

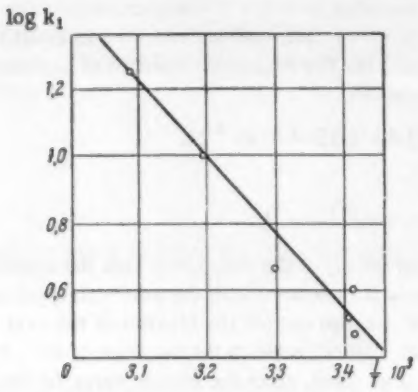


Fig. 5. Relationship between the rate constant of the reaction of carbobenzoxyglycine with CME-carbodiimide and the temperature.

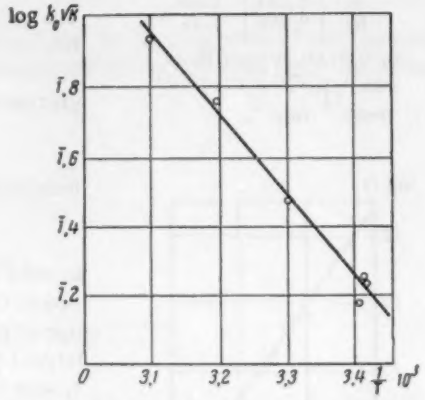


Fig. 6. Relationship between the effective rate constant of the acid-catalyzed hydration of CME-carbodiimide and the temperature.

than in 50% dioxane or tetrahydrofuran. The reaction product is stable in neutral and acid medium and is hydrolyzed in alkaline medium. It is not the anhydride of carbobenzoxyglycine and is most probably N-(carbobenzoxyglycyl)-CME-urea.

2. In accordance with existing theories of the mechanism of reactions involving carbodiimide derivatives, N-(carbobenzoxyglycyl)-CME-urea is obtained as a result of the isomerization of a labile intermediate ester of carbobenzoxyglycine and the enolic form of the urea. The formation of the latter is the limiting stage of the reaction. Measurement of the kinetics of formation of N-(carbobenzoxyglycyl)-CME-urea thus gives the rate of activation of the carboxyl group of carbobenzoxyglycine.

3. The formation of activated carbobenzoxyglycine is accompanied by the parrallel consumption of CME-carbodiimide as a result of the acid-catalyzed hydration of CME-carbodiimide.

4. The rate constants and activation energies of the parallel reactions of carbobenzoxyglycine activation and acid-catalyzed hydration of CME-carbodiimide have been determined. The rate constant of the activation is equal to

$$k_1 = 3{,}9 \cdot 10^6 e^{-\frac{10500}{RT}} \text{ liter} \cdot \text{mole}^{-1} \cdot \text{sec}^{-1}$$

The effective activation energy of the acid-catalyzed hydration of CME-carbodiimide is 10.7 kcal/mole.

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All abbreviations of periodicals in the above bibliography are letter-by-letter transliterations of the abbreviations as given in the original Russian journal. *Some or all of this periodical literature may well be available in English translation.* A complete list of the cover-to-cover English translations appears at the back of this issue.

EFFECT OF THE SOLVENT ON THE REACTIVITY AND OTHER PHYSICO-CHEMICAL CHARACTERISTICS OF POLAR PARTICLES

I. KINETICS OF SOLVOLYSIS OF TERTIARY BUTYL CHLORIDE IN TWO- AND THREE-COMPONENT SOLVENTS

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The following methods are proposed for studying the kinetics of solvolysis of $(CH_3)_3CCl$: a highly sensitive conductometric method with oscillographic display, a method of titrating the reacting solution directly in the reaction vessel, and also a method of calculating the reagent distribution which permits simultaneous determination of the rate constants and the activity coefficients of tertiary butyl chloride in systems not in thermodynamic equilibrium.

According to the Ingold-Hughes hypothesis [1-3], the unimolecular solvolysis of tertiary butyl chloride includes a slow stage of alkyl halide ionization:

$$(CH_3)_3CCl \xrightarrow[\text{slow}]{} (CH_3)_3C^+ + Cl^-$$

$$(CH_3)_3C^+ \xrightarrow{\text{fast}} (CH_3)_2C{=}CH_2 + H^+ \qquad \text{(E1)}$$

$$(CH_3)_3C^+ \xrightarrow[\text{fast}]{H_2O} (CH_3)_3COH + H^+. \qquad \text{(Sn1)}$$

in which the carbonium cation formed reacts quickly with a nucleophilic reagent (H_2O, OH^-, etc.), giving substitution products (Sn1 reaction), or is stabilized, a proton being split out (E1 reaction).

This reaction became the subject of many investigations after the work of Hughes [4], who showed that its specific rate in aqueous-alcoholic solutions, in conformity with the ionization hypothesis, does not depend on the pH of the medium, but increases considerably with the concentration of water in the solvent.

Later Bateman and Hughes [5] showed that the reaction can occur even in nonaqueous solutions. They studied the reaction in the solvent formic acid, which has great ionizing power, and found that small admixtures (up to 10%) of water have practically no effect on its rate, although in this case the product composition and the equilibrium position in the system vary widely. This reaction was further studied in ammonia, alcohols, acetic anhydride, nitromethane, formamide, and dimethylformamide, in aqueous solutions of alcohols, acetone, dioxane, and acetic acid, in a number of nonaqueous mixed solvents, and in other media.*

It must be noted that the arguments of Ingold and Hughes in favor of the ionization mechanism of this reaction were not sufficient to solve the question as to its true molecularity owing to the known difficulty of distinguishing the influences of the solvent as an external field (medium) and as a reagent. Many authors, including Olson and his co-workers [8], Hammett and Farinacci [9], Glasstone, Laidler, and Eyring [10], Prevost [11], Ross and Labes [12], Swain and co-workers [13], and Ya. K. Syrkin [14], consider the reaction to be bimolecular, trimole-

* The most complete summary of rate constants of the reaction in two-component solvents is given in [6]; that in individual solvents is given in [7].

cular, or polymolecular; it is suggested that one or more molecules of water (or other active solvent) enter into an activated complex and thereby promote cleavage of the C–Cl bond. However, these hypotheses have not received enough experimental confirmation.

The great interest of this reaction is explained primarily by its key position in the system of organic substitution and splitting-out reactions.

Although the discussion of its detailed solvolytic mechanism and the causes of the pronounced effect of the medium on its rate is still far from closed, it becomes more and more obvious that in the case of $(CH_3)_3CCl$ decomposition, which is one of the least complicated reactions, the solution of these questions opens the way to understanding of the nature of other solvolytic reactions.* On the other hand, the accumulation of data on the rates of uncomplicated reactions in various solvents facilitates the development of our ideas in one of the most difficult and theoretically little-studied fields – the problem of polar interaction of dissolved particles and the solvent.

Systematization and analysis of data on effects of the medium [7], shows that the question of the solvent's effect on reaction rates is not an isolated, specific problem. In recent years new regularities have been established which relate the rate constants of $(CH_3)_3CCl$ solvolysis to the polar and physical properties of the pure solvents, their solvent power, and their effect on ionic mobilities [7, 17] and on the spectra of the polar particles [18-20]. Somewhat earlier [6, 21-23] a relation was established between the rate of $(CH_3)_3CCl$ solvolysis and the rates of conversion of other alkyl halides. The author of the present article [17] noted the possibility of quantitatively calculating nonspecific polar effects of the medium, within the bounds of the theory of regular solutions.

It is extremely desirable to further extend investigations in this direction in order to perfect kinetic methods, to include a greater number of solvents, to discover new regularities, and to develop methods for quantitatively calculating effects of the medium.

Certain questions of method and the results of investigation of the solvolysis kinetics of tertiary butyl chloride in two- and three-component solvents, are discussed in the present article.

1. Method of Internal Titration

The rate of decomposition of $(CH_3)_3CCl$ does not depend on the pH of the medium, which makes it possible to investigate this rate by the method of titration by alkali, directly in the reaction vessel, of the hydrochloric acid formed in the reaction. Bearing in mind the peculiarities of the method (titration of the** entire mass of reacting solution instead of small samples, the possibility of exact fixing of time intervals between successive instants of neutralization, investigation of the reaction under conditions of irreversibility, etc.), which make it considerably different from the usual method of sample titrations, we investigated the sources of errors and found that it could be used to obtain rate constants in the interval $10^{-6} < k < 10^{-3}$ sec^{-1} with an accuracy within ±1.5%. Since our procedure differs from that used by Swain in that it takes into account the effect of distribution of the reagent between gas and liquid and makes it possible to find not only the rate constants, but also the activity coefficients of the reagent, we shall consider certain details of it.

In the experiments we used $(CH_3)_2CCl$, purified by rectifying twice in a standard meter colum: t_b = 50.8--50.9°, n_D^{25} = 1.3868. The purity of the solvents was checked by density and refractive-index determinations.

The measurements were carried out in an assembly consisting of a flask, placed in a thermostat (±0.01°), and a 2-ml pipet, the liquid level in which was measured with an accuracy within ±0.001 ml. The pipet ended in a long, thin capillary which did not reach the solution surface. The titrating solution was prepared by dissolving Na or NaOH in the medium under investigation. Several drops of bromthymol blue indicator were dried in the reaction vessel before the latter was filled. Each time, a slight excess of alkali was added, which then was

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*Let us note that in the $(CH_3)_3CCl$-solvolysis reaction the same "indifferent-solvent effect" appears, as was discovered by N. A. Menshutkin in the case of reactions between alkyl iodides and tertiary amines [15, 16]. In the case of $(CH_3)_3CCl$ solvolysis the Menshutkin effect is more pronounced and less complicated by various specific factors.

**This principle was first used by Peters and Walker [24] and then by Swain and his co-workers [25, 26], to determine the solvolysis kinetics of certain halide compounds with an accuracy within ±6% [25]. With respect to $(CH_3)_3CCl$ solvolysis this method was used [26] only to estimate approximately the half-period of the reaction in an aqueous solution containing 5% acetone.

uniformly neutralized by the HCl formed in the reaction. This made it possible to fix precisely (within ±0.2 sec) the time intervals between successive instants of neutrality of the solution, at which the latter assumed a green color corresponding to the color of the liquid in a comparison flask. The procedure was repeated until the rate had decreased to 10-12.5%.

Since the level φ of the alkali solution in the pipet was a linear function of the concentration of the acid formed in the reaction, the kinetic equation may be written in the form:

$$\frac{d\bar{\tau}}{d\tau} = k_{app}\varphi + \text{const},$$

where k_{app} is the apparent rate constant in the given experiment.

The constants are calculated from the data ($\Delta\varphi_i$, $\Delta\tau_i$) by differential methods based on calculation of the deviations of the average velocities $\Delta\varphi/\Delta\tau$ from their instantaneous values $d\varphi/d\tau$. This method was considered in detail in [27]. No parameters need be known for this calculation.

2. Conductometric Method with Oscillographic Display

We also developed a highly sensitive conductometric method for investigating reaction kinetics in a cell with smooth platinum electrodes, i.e., under conditions of high polarization. The bridge diagonal (Fig. 1) was an oscillographic unit consisting of voltage amplifier A_1, an Étalon EO-7 oscillograph, commercial-frequency filter F, and the four-stage resonance amplifier A_2 of an INO-3M oscillograph; the tube T_2 of this instrument was the final visual indicator. The low-gain section A_1-A_3-T_1 served for rough indication, and also to check the composition of the diagonal signal. The sweep voltage on tube T_2 was supplied directly from the generator. In this case, owing to the low input impedance of the oscillograph, leakage occurred, which was compensated by inserting resistance r_c and capacitance C_c in the left branch of the generator output. To minimize the effect of inductive and capacitive connections, a scheme of measurements "in one arm" was used. In this case standard resistance box r_4 and variable inductance (variometer) L were connected in series with cell x. With key K closed, zero balance was first established with r_4 = 10,000 ohms and L = 0, by means of box r_3. When the cell was connected, its resistance was deducted from r_4, and the cell capacity was compensated by variometer L. This scheme permits both stationary single measurements and kinetic investigations with time-invariant arm resistances.

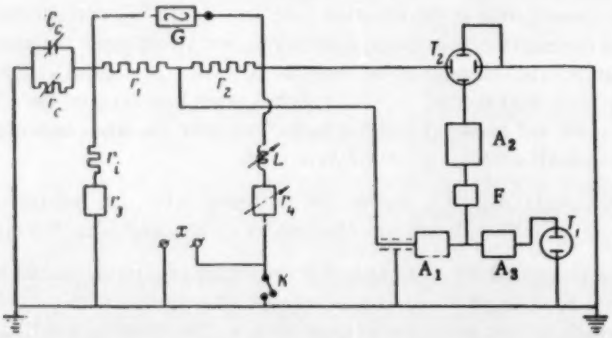

Fig. 1. Conductometric assembly for investigation of reaction kinetics: G—ZG-10 generator; r_1, r_2—ratio arms $r_1 = r_2$ = ohms; L—Étalon VR-G variometer; r_4—knob-type resistance box; r_3, r_i—resistance boxes; x—cell; C_c—variable capacitor, 1000 μμf; r_c—potentiometer, 3 Mω; A_1, A_2, A_3—amplifiers; T_1, T_2—oscillograph tubes; F—commercial-frequency filter.

Precise control is achieved in this setup. Near bridge equilibrium, unbalance of the resistive component causes only broadening of the ellipse on the screen of T_2, whereas a change in the reactive component causes only rotation of the figure. From the form of the figure, therefore, it could be directly determined which of the bridge elements to regulate, and in which direction, in order to restore the balance. Ideal (top row) and observed (bottom row) figures on the screen of T_2 are shown in Fig. 2 in natural size. Note that the ohmic balance, corres-

ponding to Fig. 2b, is equal to 0.005%. The possibility of carrying out measurements in the presence of a considerable background of residual noise (light field), appreciably increases the sensitivity of the method: the amplitude of the minimum distinguishable signal of bridge unbalance at a frequency of 1000 cycles is about one-fifth of the noise level.

Kinetic measurements were carried out in a special reaction vessel whose main reservoir was geometrically remote from the cell with the electrodes; rotation of the stirrer (rotor) caused the solution under investigation to circulate rapidly through the reservoir and cell. This "cell and turbine," proposed by the author in [28], proved very convenient for exact kinetic measurements.

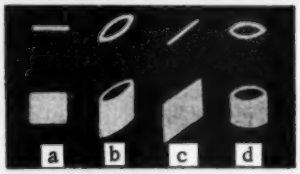

Fig. 2. Theoretical (top) and real (bottom) figures on the screen of tube T_2 near bridge equilibrium: a) Full balance; b) both components unbalanced; c) only the reactance unbalanced; d) only the resistance unbalanced.

On investigating the kinetics we noted the time of onset of bridge equilibrium with a preset excess resistance in the substitution box r_4, which made it possible to fix experimental intervals with sufficient accuracy and as often as desirable for following the process. The rate constants were calculated directly from resistance–time data by differential methods. Calculation of constants and calibration are discussed in [27]. Typical kinetic straight lines also are given there.

3. Investigation of Reaction Kinetics Under Conditions of Distribution of the Reagent

Results of the first measurements in aqueous-alcoholic solutions showed a dependence of k_{app} on the volume of liquid in the reaction vessel, and certain other anomalies, which, allowing for the high volatility of $(CH_3)_3CCl$ under the given conditions, could naturally be explained by distribution of the reagent between gas and solution in the course of the experiment. In the works of Hughes [4,5], Olson [8, 29], and Swain [26] and the first works of Winstein [21] this phenomenon was not taken into account. In a recent work Fainberg and Winstein [22], in order to avoid complications due to reagent volatility, completely excluded the gas phase from the reaction. It was of interest to us to use another more general method of investigating kinetics which quantitatively allows for the distribution effect. It proved possible by this method to obtain not only the true rate constants, but also data on the coefficients of distribution of the reagent in the nonequilibrium systems being studied.

Typical data, obtained by the internal-titration method, are given in Fig. 3 and Table 1. Evidently the gradients of the kinetic straight lines at a given temperature in a given solvent vary (from $717 \cdot 10^{-6}$ to $1135 \cdot 10^{-6}$ sec^{-1}) with respect to the ratio (λ) of the gas-phase volume in the reaction vessel to the solution volume, the constants increasing as the gas-phase volume decreases.

In using the conductometric method the reaction rate was found to depend on whether the solution was stirred. Data for the reaction in dioxane-water solution (55.0 wt.% water) at 25.0° are shown in $\dot{\varphi}-\varphi$ coordinates in Fig. 4. The experiment was performed without stirring from the starting point φ_0 to point φ^* (straight line I), and with stirring from point φ^* on (straight line II). A break in the kinetic straight line is observed on change of conditions: as was to be expected, straight line I and the continuation of straight line II intersect at a point with the abscissa φ_0. Evidently the rate constant (slope of the straight line) is greater in the experiment without stirring than in the same experiment with stirring. Under these conditions cessation of stirring is equivalent to elimination of the gas phase.

A simple calculation, based on the currents noted in the reaction vessel, leads to the equation

$$k_{app}^{-1} = k^{-1} + k^{-1} \cdot \alpha \cdot \lambda; \quad \alpha = \frac{C_g}{C_l}; \qquad \lambda = \frac{V_g}{V_l}, \tag{2}$$

where k is the true rate constant; α is the reagent distribution coefficient; C and V denote the concentrations and volumes, respectively, for the liquid (index l) and gas (index g) phases.

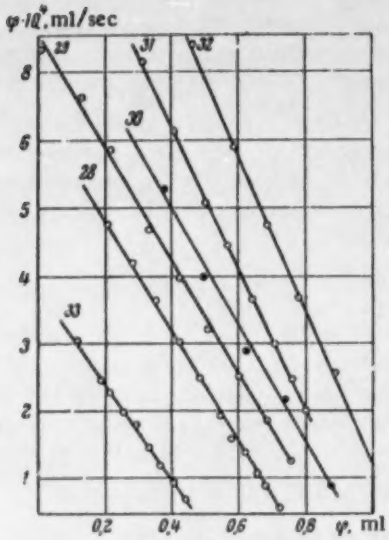

Fig. 3. Kinetic straight lines of the reaction in ethanol-water solution (63.83 wt. %) at various values of λ, 25.0°. The numbers of the straight lines correspond to the numbers of the experiments. In Experiment 30, because of the high rate (straight line 30 is shifted 10.5 scale units downward along the axis of ordinates), the intervals $\Delta\tau$ were only 1-1.5 min, which resulted in larger errors.

TABLE 1

Solvolysis of $(CH_3)_3CCl$ in Ethano - Water Solution (63.83 wt. %) at 25.0°

Experiment No.	$C_0 \times 10^3$, moles·sec^{-1}	λ	$k_{app} \times 10^6$, sec^{-1}
33	3,66	2,77	717
28	3,00	1,90	814
29	5,86	1,83	830
30	8,72	1,64	865
31	1,99	0,68	1046
32	3,00	0,39	1135
Graphical extrapolation		0	1250

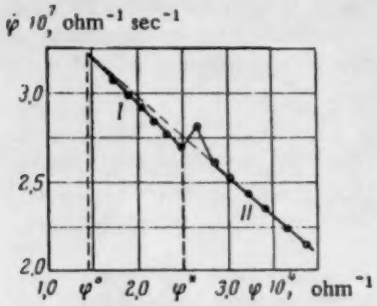

Fig. 4. Kinetic straight line with a break: I) The process without stirring; II) the process with stirring; φ_0 – corresponds to the solution resistance before the reaction $\left(\varphi = \frac{10000}{R - R_C}\right.$, R is the solution resistance, and R_C is a semi-empirical calibration constant [27]$\left.\right)$

According to (2), the inverse value of k_{app} should be a linear function of λ; the segment cut off by the straight line (in $k_{app}^{-1} - \lambda$ coordinates) on the axis of ordinates should be equal to k^{-1}, and the angular coefficient of the straight line should be αk^{-1}; hence $\alpha = k \frac{\partial k_{app}^{-1}}{\partial \lambda}$. Formula (2) was found to be applicable in all cases. The results of investigating the kinetics at various values of λ are given in Table 1. Kinetic straight lines of this series are shown in Fig. 3; values of k_{app} are given in the last column of Table 1, and in $k_{app}^{-1} - \lambda$ coordinates in Fig. 5.

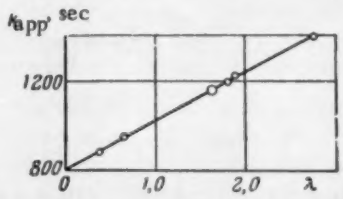

Fig. 5. Relation between k_{app}^{-1} and λ.

Evidently all the points, encompassing a 7-fold range of variation of λ, lie very close to a straight line. A 4.5-fold change in the initial (total) reagent concentration C_0 does not affect the distribution coefficient α, as is naturally to be expected at low solution concentrations – 10^{-2}-10^{-3} mole/kg. From the data of Fig. 5 we find $k = 1250 \cdot 10^{-6}$ sec^{-1} and $\alpha = 0.273$. This result, inter alia, means that in Experiment 32 more than 40% of the reagent was present in the gas phase. Thus both the true rate constant and the reagent distribution coefficient may be found from the data for a group of experiments at various values of λ. The coefficient α is directly related to the activity coefficient of the reagent, γ_1:

$$\gamma_1 = \frac{1}{P_0}\left(\frac{P_1}{N_1}\right)_{N_1 \to 0} = \alpha \frac{1000RT}{P_0 V_0}, \qquad (3)$$

where P_0 is the vapor pressure of pure $(CH_3)_3CCl$; P_1 is the vapor pressure of $(CH_3)_3CCl$ in solution, with the mole fraction N_1; V_0 is the molar volume of the solvent. The proposed method makes possible a kinetic approach to the problem of measuring this important characteristic of the state of the substance in various media.

4. Experimental Results

Aqueous Ethanol Solutions. Data, obtained by internal titration, are given in Table 2. Rate constants in solvents containing more than 20% water were determined from a group of experiments (from 3 to 6) at various values of λ. In "slower" solvents the effect of distribution was negligible. Our data, obtained under conditions of distribution, agree well with the results obtained when the reaction vessel was completely filled with the solution (Fig. 6). Values of α, obtained by the kinetic method, are compared with the results of Olson and Halford's direct measurements [8] in Fig. 7. These authors used the ordinary stationary Henry method (measurement of the vapor pressure over the solution with respect to the solution concentration); however, they overlooked the fact that, owing to the reaction of $(CH_3)_3CCl$ in the liquid phase, its vapor pressure must be greater than the equilibrium value. Hence in systems with a high water concentration, where the reaction rate is high, the stationary method should show high results. Evidently, when α is small, values obtained under stationary conditions agree with our results, whereas when α is large, they deviate substantially. When the kinetic method is used, equilibrium is continuously maintained in the system, and therefore our method is free from the indicated shortcoming.*

TABLE 2

Values of k and α in Ethanol-Water Solutions

Water content wt. %	25,0° $k \cdot 10^6$ sec^{-1}	25,0° α	30,0° $k \cdot 10^6$ sec^{-1}	30,0° α	Water content wt. %	25,0° $k \cdot 10^6$ sec^{-1}	25,0° α	30,0° $k \cdot 10^6$ sec^{-1}	30,0° α
7,46	0,548	—	1,095	—	52,13	262	0,065	496	0,094
12,05	1,44	—	2,86	—	53,49	308	0,067	608	(0,09)
15,5	2,62	—	—	—	54,84	366	0,06	—	—
28,88	17,5	0,01	32,8	0,02	56,83	482	0,099	865	0,101
47,64	158	0,049	298	0,08	63,83	1250	0,273	—	—

TABLE 3

Values of k and α in Ethylene Glycol and Its Aqueous Solutions

Wt. % of water	t°	$k \cdot 10^6$ sec^{-1}	α	Wt. % of water	t°	$k \cdot 10^6$ sec^{-1}	α
0	25,0	24,9	0,048	15,5	30,0	343	0,28
0	30,0	50,6	0,11	27,7	25,0	625	0,28
7,4	25,0	63,5	0,12	35,7	25,0	1280	0,63
15,5	25,0	175	0,20	35,7	30,0	2410	0,89

Ethylene Glycol and Its Aqueous Solutions. Results are given in Table 3 and shown in Fig. 6. This system has not been investigated before. Values of k and α for pure ethylene glycol agree with data for other pure liquids [17]**.

* The sensitivity of the kinetic method is low for values of α less than 0.05; in this case the Henry method is preferable.

** In [17] it was shown that the values of k and α for individual solvents conform to the relation $\lg k = c_1 + c_2\sqrt{\lg \gamma_1}$; γ_1 is related to α by formula (3). This relation is one of many conclusions of a theory based on the regular-solution method. In a forthcoming article of this series the calculation of reaction rates with respect to the medium will be discussed.

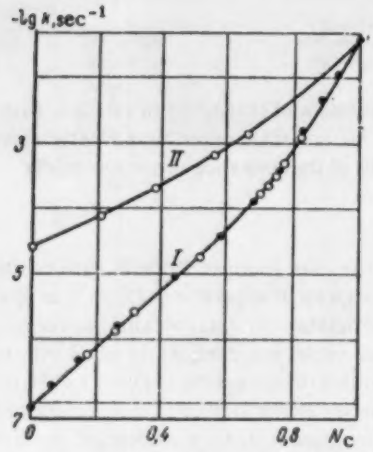

Fig. 6. Reaction rate constants for the solvolysis of $(CH_3)_3CCl$ in ethylene glycol-water (I) and ethanol-water (II) solutions at 25.0°: The dots denote Fainberg and Winstein's data [6], obtained in a reaction vessel completely filled with the liquid phase; the circles denote our data obtained under conditions where the reagent was distributed between solution and gas.

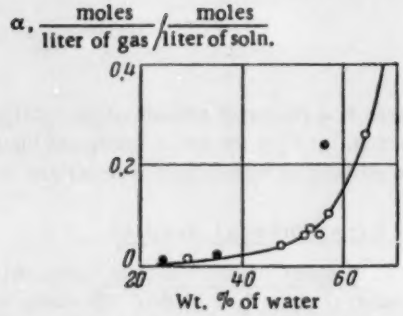

Fig. 7. Relation between the $(CH_3)_3CCl$ distribution coefficient and the composition of the ethanol-water solution, at 25°: The circles denote our results; the dots denote Olson and Halford's data [8].

Glycerol. The reaction in pure glycerol is complicated mainly by two effects: The high viscosity of the solvent sharply reduces the efficacy of stirring and the accuracy of dosage, and the appreciable salt effect leads to bending of the straight lines. Exact dosage of alkali was replaced by counting of drops. Average result of three experiments: $\underline{k} = (80 \pm 20) \cdot 10^{-6}$ sec^{-1} at 25°.

Liquid $(CH_3)_3CCl$. In order to make certain calculations it was necessary to determine approximately the reaction rate in the pure liquid. For this purpose the reaction rate was measured at 100° by the ampule method. The maximum degree of conversion was 3%; in this case the reaction rate $\Delta P/\Delta\tau$ was proportional to the weight of the reagent, P. Average result of ten measurements: $\underline{k} = (2 \pm 0.5) \cdot 10^{-6}$ sec^{-1}. Assuming that the pre-exponential factor is equal to the theoretical value, 10^{13} sec^{-1}, we find log k = 10.4 ± 0.5 sec^{-1} at 25°. The value of log $\underline{k}$, estimated in this way for pure, liquid $(CH_3)_3CCl$, agrees well with data for other liquids [17].

5. Investigation of the Effect of Small Admixtures of Various Liquids on the Reaction Rate in a Standard Solvent

With respect to their effect on the rate of solvolysis of $(CH_3)_3CCl$, solvents may be arranged in a definite order: the most "active" of the liquids studied is water, and the least "active" is dioxane [7]. It was of interest to confirm these data by some other route, simpler than measuring the rates in the pure, individual media.

Such results may be obtained by the method of small additions. Data are given in Fig. 8. Every point on this graph, except the nodal point, is the result of one experiment with the reaction vessel filled as completely as possible with the solvent. More precise values of the constants were determined by means of formula (2).

According to the data of Fig. 8, the "activity" of the given solvents decreases in the following order: water > glycerol > ethylene glycol > methanol > ethanol > tert-butyl alcohol > methyl ethyl ketone > dioxane > chloroform > benzene. This series agrees with the order of rate constants in the pure added liquids [7]. Hence the limiting slope of each curve may serve as a measure of the activity of the pure added liquid. By using this method, reaction rates can be estimated in such slightly active media as benzene, in which direct measurement is difficult.

I sincerely thank Corresponding Member, Acad. Sci. USSR, V. V. Voevodskii and Academician M. I. Kabachnik for their interest in the work and its discussion.

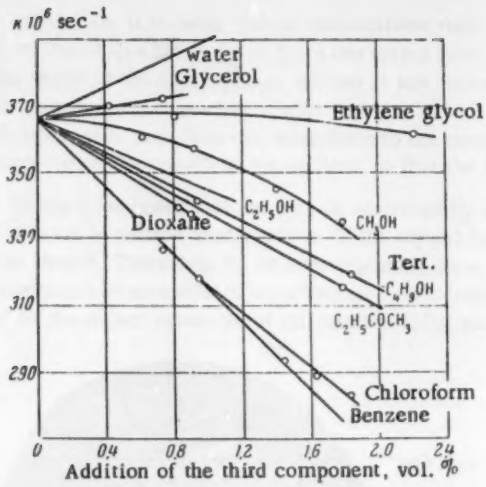

Fig. 8. Effect of additions of a third component to the ethanol-water (54, 84 wt. %) solution on the specific reaction rate at 25°. Method of internal titration.

SUMMARY

1. A method is proposed for studying the solvolysis of $(CH_3)_3CCl$ under conditions where the reagent is distributed; this method makes it possible to find both the true reaction rate and the distribution coefficient of the reagent simultaneously from kinetic-measurement data.

2. A highly sensitive conductometric method was developed for the kinetic investigation of reactions under conditions of strong electrode polarization, which includes oscillographic display, measurements in one arm, inductive compensation of electrode capacitance, and the use of a "cell and turbine."

3. Rate constants and distribution coefficients were measured in the solvents water-ethylene glycol and water-ethanol at 25.0° and 30.0°. Reaction rates were approximately determined in glycerol and pure $(CH_3)_3CCl$.

4. It was shown that the effect of small additions of of various liquids on the reaction in a "standard" solvent varies in the same direction as the effect of the pure added liquids.

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SHAPE OF NUCLEI IN THE DEHYDRATION OF ZINC SULFATE HEPTAHYDRATE

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It is shown that the shape of the nuclei in the dehydration of zinc sulfate heptahydrate depends on the dehydration conditions. If the dehydration takes place at low temperature and low water-vapor pressure, rectangular nuclei are formed. At higher temperatures and water-vapor pressures rounded nuclei are formed. The results obtained are explained from the point of view of the catalytic effect of the solid reaction product formed on dehydration.

It was shown by W. Garner and co-workers [1, 2] that the shape of the nuclei in the dehydration of cupric sulfate pentahydrate depends on the water-vapor pressure over the crystal hydrate. If dehydration takes place at a low water-vapor pressure (in vacuo), star-shaped product nuclei are formed. On increase of the water-vapor pressure, they are converted to rounded nuclei.

G. V. Sakovich and V. V. Boldyrev [3] proposed the following explanation of this phenomenon: An amorphous solid product is formed on dehydration in vacuo. Since the product has no crystal lattice of its own, the conditions of development of the nucleus and its shape are determined mainly by the structure and anisotropy of the lattice in the original substance. On increase in the pressure of water vapor, whose presence facilitates transition of the product from the amorphous to the crystalline state [4, 5], the product forms its own crystal structure. As a result the shape of the nucleus changes, since it begins to depend less on the crystal structure of the original substance and more on that of the product, owing to the catalytic action of the latter.

Our recent experiments in observation of the shape of nuclei formed in the dehydration of zinc sulfate heptahydrate at various temperatures and humidities of the atmosphere over the crystal hydrate confirm the hypotheses, advanced in [3], on the dependence of the shape of nuclei on the dehydration conditions.

The experiments were performed in an apparatus in which the formation and growth of crystal nuclei on dehydration of crystal hydrates at specified atmospheric humidities and temperatures could be observed under the microscope. A detailed description of the apparatus is given in [6].

It was found that if the dehydration is carried out at low temperatures (5-10°) and low humidities of the air over the crystal hydrates (1.1-1.3 mm), rectangular nuclei are formed (Fig. 1).

Cracks, characteristic of the process of crystallization of the solid product, were not observed.

In the further course of the process the nuclei become rounded.

When the water-vapor pressure is increased to 4.2 mm and the temperature to 35°, rounded nuclei appear, having deep radial cracks, which indicate crystallization of the solid product (Fig. 2).

In this case it is noted that at temperatures from 15 to 45° and humidities from 1.5 to 4.2 mm the eccentricity of the ellipse increases as the water-vapor pressure over the crystal-hydrate surface decreases. We suggest that the shape of the heptahydrate nucleus at low vapor pressures is determined by the latticestructure in the original substance. As the water-vapor pressure increases, as shown in [5], the dehydration product of zinc sulfate heptahydrate goes over from the amorphous to the crystalline state, and the orienting action of the product lattice is superposed on the growth of the nucleus, so that the latter grows more isotropically.

It should be noted that the picture described by us is observed only in heptahydrate crystals containing a small number of surface macrodefects. If the crystal has a defect surface, rectangular nuclei are not formed in the first instant. Therefore, for an unambiguous answer to the question as to when the shape of the nuclei formed on dehydration of zinc sulfate heptahydrate is determined by the state of the solid product, and when it is determined by the defect character of the lattice, additional investigations are required in each concrete case.

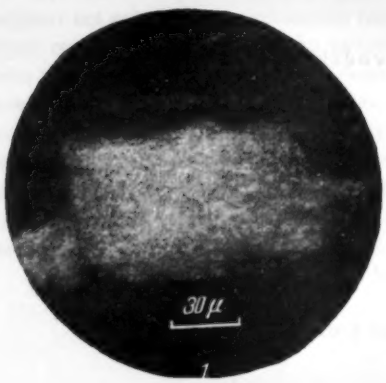

Fig. 1

Fig. 2

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A STUDY BY THE ELECTRON PARAMAGNETIC RESONANCE METHOD OF THE PROPERTIES OF HYDROGEN ATOMS ON THE SURFACE OF SILICA GEL

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A study has been made of the annealing of hydrogen atoms formed during the low-temperature irradiation of silica gel with γ-rays.

It has been shown that between -100° and -150° the adsorbed hydrogen atoms react with ethylene and oxygen.

Livingston, Zeldes, and Taylor [1], and Bubnov, Voevodskii, Polyak, and Tsvetkov [2] have found that when glasses and silica gel are irradiated with γ-rays at the temperature of liquid nitrogen, hydrogen atoms are formed from the molecules of adsorbed water or the surface OH-groups; these hydrogen atoms can be detected by the electron paramagnetic resonance (EPR) method.

The present communication is devoted to a study of the properties of the hydrogen atoms adsorbed on the surface of silica gel.

Specimens of silica gel with a surface area of 300 m^2/g were evacuated for 10 hours at 425° to a pressure of 10^{-5} mm Hg and irradiated in vacuo at the temperature of liquid nitrogen by γ-rays from a Co^{60} source. The radiation dose amounted to approximately 10 megarad. The EPR spectra were recorded at the temperature of liquid nitrogen on an EPR spectrometer with high-frequency modulation of the magnetic field [3].

Figure a gives the spectrum of the irradiated silica gel. The central signal is produced by the radicals or defects formed when hydrogen atoms are removed from the silica gel under the influence of the γ-rays. On both sides of the central signal lie the components of the hydrogen doublet. The splitting between the components of the doublet is 506 oe, and the g-factor is close to the g-factor of a free electron. The width of the components of the doublet between the points of maximum slope in vacuo is equal to 1 oe. The signal is appreciably saturated under the influence of superhigh-frequency power.

At the temperature of liquid nitrogen, the signal of the hydrogen atoms in vacuo remained unchanged for an almost unlimited time. When the temperature was increased to between -150° and -110°, the signal of the hydrogen atoms was found to decrease with time, obeying the first order equation. This is apparently due to the disappearance of hydrogen atoms as a result of their reaction with "traps" on the silica gel surface. If the hydrogen atoms had recombined in pairs, the decrease in the signal would have shown second order kinetics. The following expression was found for the rate constant for the reaction involved in the disappearance of the hydrogen atoms

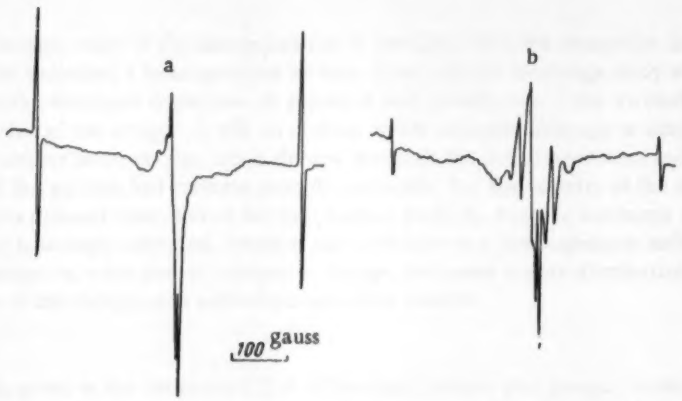
$$k = 10^{-1} \cdot e^{-2000/RT}\ sec^{-1}.$$

The low value of the pre-exponential factor of the rate constant should be noted. The surface diffusion of the hydrogen atoms is evidently associated with considerable steric hindrance.

In an atmosphere of oxygen, the saturation of the signal of the hydrogen atoms at the temperature of liquid nitrogen is removed.

The rate of annealing of the hydrogen atoms is also altered at higher temperatures. Thus at -130° the initial rate of recombination of hydrogen atoms in the presence of oxygen is three times the rate of their recombination in vacuo. An even greater difference is observed when the hydrogen atoms are annealed in the presence of ethylene adsorbed on the silica gel surface. Thus measurements carried out at -150° showed that the rate of annealing of hydrogen atoms in the presence of ethylene is 30 times the rate of annealing in vacuo.

The results obtained can be explained as follows: in the presence of oxygen or ethylene the hydrogen atoms disappear not only by a recombination reaction as is the case in vacuo, but also by reaction with molecules of oxygen or ethylene adsorbed on the surface. This leads to an increase in the rate of disappearance of hydrogen atoms in oxygen or ethylene. This viewpoint is also confirmed by the fact that when the hydrogen atoms were annealed in the presence of ethylene adsorbed on the silica gel surface, we observed a change in the nature of the central part of the spectrum of the irradiated silica gel. This is illustrated in Fig. b, which gives the spectrum obtained after a 30-second exposure of a specimen with ethylene adsorbed on its surface, at a temperature of -150°. The intensity of the hydrogen signals has decreased sharply, and on the central signal, on both sides of the original line, further components resembling the spectrum of the ethyl radical have appeared. The splitting between these additional components is equal to approximately 22 oe.



The chemical reaction taking place may be described by one of the following equations:

$$\dot{SiO} + C_2H_{4ads} \longrightarrow SiO \cdot C_2H_4 \qquad (1)$$

or

$$H_{ads} + C_2H_4 \longrightarrow C_2H_5\ ads \qquad (2)$$

Reaction (2) appears to us more probable, for the following reasons. Firstly, the rate of annealing of the hydrogen atoms in the presence of ethylene is much greater than the rate of annealing in vacuo. Secondly, when the hydrogen atoms were annealed beforehand in vacuo and the specimens then brought into contact with ethylene and kept in contact with ethylene at a temperature of -150°, no additional signal was produced.

The results which we have obtained show that the hydrogen atoms adsorbed on silica gel have a high reactivity.

Further studies will show whether active products of this type play a part in low-temperature catalytic reactions.

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AN ISOTOPIC STUDY OF THE SURFACE HETEROGENEITY OF OXIDE CATALYSTS FOR THE DECOMPOSITION OF ISOPROPYL ALCOHOL

II. ALUMINUM AND ZINC OXIDES

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A differential isotopic study of the decomposition of iso-C_3H_7OH in the adsorption layer on aluminum oxide indicated a heterogeneous surface. In an isotopic exchange study on an Al_2O_3 surface with subsequent desorption, it appeared that dehydration of the alcohol occurred on a small fraction of the surface (4-6%) on centers, where isotopic exchange is inhibited. A differential isotopic study on zinc oxide showed that both the dehydrogenation and dehydration products of the alcohol had constant specific activities, but the activity of the dehydrogenation products differed from that of the dehydration products. Isotopic exchange of iso-C_3H_7OH on ZnO is strongly inhibited, which is characteristic of a heterogeneous surface. A study of the desorption, after partial isotopic exchange, indicated a wide distribution in activation energies of the dehydration and dehydrogenation centers.

Results have been given in the literature [1] of differential isotopic and isotopic exchange investigations of the calcium oxide surface. It was of interest to compare the properties of this typical basic oxide with the properties of an acidic oxide—aluminum oxide and a typical electron semiconductor oxide—zinc oxide. Out of the literature data on studies of the surface heterogeneity of these catalysts, we noted the experiments of Keier [2], which were mentioned in the preceding paper, the experiments of Babushkin and Uvarov [3], who discovered three types of centers on Al_2O_3 for adsorption of ethyl alcohol, and the experiments of Vasserberg and Balandin [4] on the differential blocking of active Al_2O_3 centers for decomposition of alcohols.

Aluminum Oxide

Figs. 1 and 2 contain experimental results of a differential isotopic study of the decomposition of iso-propyl alcohol on aluminum oxide. The experimental method was analogous to that described earlier [1] for calcium oxide, but no dehydrogenation was observed on Al_2O_3. The alcohol is preferentially decomposed by dehydration. The amount of aluminum oxide was 3 g and the specific surface area 460 m^2/g. In one experiment (Fig. 1) unmarked alcohol was adsorbed first, then marked; in the other experiment (Fig. 2) this adsorption sequence was reversed. It can be seen from these Figures that the activity of all the desorbed fractions is approximately constant and approximates to the mean activity of the alcohol on the surface. At high temperatures (higher than 325°), as in the case of calcium oxide, a decrease in activity is observed which is independent of the adsorption sequence of marked and unmarked fractions. These fractions compose a very small fraction of the total amount of desorbed material (about 5%). Possible reasons for this effect were indicated in the preceding communication. It is probably due to cracking of the alcohol molecules with rupture of the C—C bond.

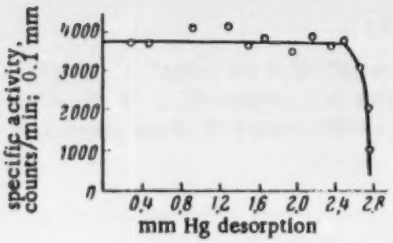

Fig. 1. Results for differential isotopic study of decomposition (dehydration) of isopropyl alcohol on Al_2O_3. Unmarked alcohol was adsorbed first, then marked.

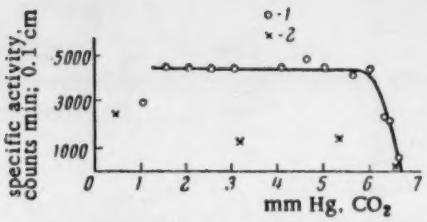

Fig. 2. Results of differential isotopic study of decomposition of iso-propyl alcohol on Al_2O_3. Marked alcohol was adsorbed first, then unmarked: 1) fractions frozen out at -195° (propylene); 2) fractions frozen out at -78°.

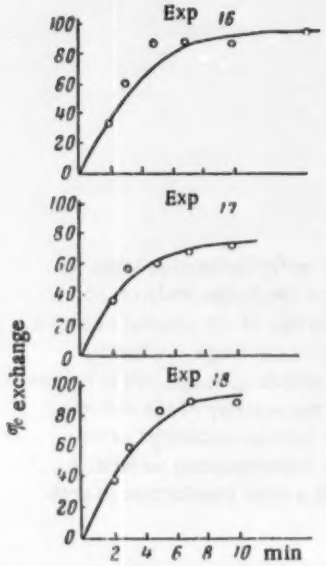

Fig. 3. Kinetics of isotopic exchange between adsorbed iso-C_3H_7OH on Al_2O_3 and iso-C_3H_7OH in the gas phase.

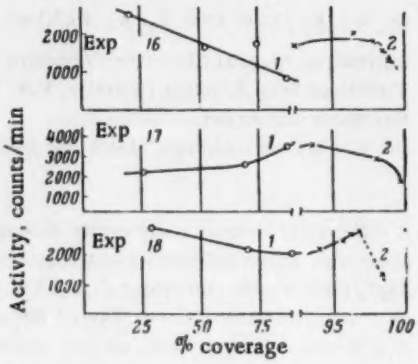

Fig. 4. Desorption (1) and dehydration (2) of iso-C_3H_7OH in the adsorption layer on Al_2O_3 after isotopic exchange. In experiments 16 and 18 marked iso-C_3H_7OH on the surface underwent exchange with unmarked iso-C_3H_7OH in the bulk; in experiment 17 unmarked iso-C_3H_7OH on the surface underwent exchange with marked iso-C_3H_7OH in the bulk.

In the experiment illustrated in Fig. 2, the activity was also measured of some fractions frozen out at -78° (dry ice). They were evidently undecomposed alcohol and products other than propylene. Their activity was considerably lower than the activity of the dehydration products; their desorption evidently occurs at centers on which the last fraction of alcohol was adsorbed (with high E adsorption), i.e., at different centers from the dehydration centers.

Further experiments on isotopic exchange with desorption, analogous to the experiments with calcium oxide were carried out. A sample of alcohol was adsorbed until adsorption ceased, and then underwent exchange with alcohol of a different isotopic composition, followed by adsorption. After the first adsorption, surface coverage of the Al_2O_3 by alcohol was about 55%, assuming the molecular area of adsorbed iso-C_3H_7OH to be 40 sq A° (see [1]). The experimental results are given graphically in Figs. 3 and 4.

Fig. 3, contains the experimental results for exchange; the abscissa axis represents time and the ordinate axis the % exhange from equal distribution, calculated from the formula:

$$\gamma = \frac{a_{in} - a_{sur}}{a_{in} - a_{sur}} \cdot 100\%,$$

where a_{in}, a_{sur} and a_{ex} are the activities of the alcohol initially, on the surface and in the bulk phase (after exchange) respectively.

Examination of the graphs shows that exchange proceeds rapidly in the first 2-5 min and then slows down. The small number of points do not enable the kinetic rule of exchange to be determined very definitely. One can only say that up to 50-70% exchange the kinetics are characteristic of a homogeneous surface [the curve can be rectified in coordinates log (1-γ), $\underline{t}$, where $\underline{t}$ is the time of exchange in min], and then exchange is suddenly retarded.

Fig. 4 contains results for a study of the isotopic composition of successive desorbing fractions of iso-propyl alcohol, desorbed after the isotopic exchange experiments presented in Fig. 3.

In experiments 16 and 18 marked iso-propyl alcohol, adsorbed on the aluminum oxide surface, underwent exchange with ordinary iso-propyl alcohol in the bulk phase. On the other hand, in experiment 17 unmarked iso-propyl alcohol on the surface underwent exchange with marked alcohol in the bulk. Results of these experiments agreed amongst themselves; the activity in experiment 17 varied in the opposite way to the variation in experiments 16 and 18.

In the desorption process, the activity of the fractions changes in the opposite direction to that direction which should result from the theory for a heterogeneous surface. For example, when the active alcohol on the surface is partially exchanged with inactive alcohol in the bulk, in the case of a heterogeneous surface and when E desorption is identical with E of isotopic exchange, the activity of the fraction should increase with increase in the temperature of desorption; in fact the reverse effect- a decrease in activity- was obtained. In all probability this effect is brought about bya so-called "topographical heterogeneity" which we observed [5] in a few cases in a differential isotopic study of the adsorption of weak acids and bases. Such topographical heterogeneity is only observed on highly porous samples, and is brought about by diffusion processes during adsorption or desorption. In the present case it can be assumed that the difficulty in exchange arises through diffusion phenomena (Fig. 3); the alcohol gets right inside the particles to the fine pores, does not participate in exchange, and is desorbed last.

Dehydration proceeds on aluminum oxide at 180-250°. The activity of the first fractions during dehydration approximates to the activity of the last fractions of desorbed alcohol; on further dehydration their activity changes, and the dehydration activation energy increases slightly. Dehydration proceeds on centers which compose about 7% of the surface initially covered by alcohol, or about 4% of the total surface. So, on the basis of these experiments, one can conclude that the dehydration reaction proceeds on a small number of regions of the aluminum oxide surface, with some variation in activity.

Finally, at 350-400° an unidentified fraction, frozen out at -78°, and which has an activity near to the activity of the last dehydration fractions, is desorbed from the aluminum oxide surface. This fraction is desorbed from centers which make up about 0.2-0.4% of the total Al_2O_3 surface.

Zinc Oxide

Fig. 5 gives the experimental results for a differential isotopic study of the decomposition of iso-propyl alcohol on zinc oxide.

The amount of ZnO was 3 g and the specific surface area 33 m^2/g. In experiment 22 a portion of ordinary alcohol was adsorbed first, then alcohol marked with C^{14}; in experiment 24 this adsorption sequence was reversed.

Fig. 5 shows the difference in activity of fractions of desorbed acetone (curve 1) and propylene (curve 2); in experiment 22 the propylene was more radioactive, in experiment 24 the acetone. This indicates that dehydrogenation and dehydration proceed on different active centers of the zinc oxide: dehydration preferentially on centers with low E_{ads}, dehydrogenation on centers with higher E_{ads}. Fractions, desorbed between 200 and 300°, had a higher radioactivity in experiment 22 and a lower radioactivity in experiment 24. The last fractions, desorbed above 300°, had a low radioactivity, independent of the adsorption sequence, as in the experiments with calcium and aluminum oxides. The reasons for this effect are probably the same as in the case of CaO and Al_2O_3.

We found earlier [6] that the selectivity of the decomposition process of iso-propyl alcohol in the adsorption layer was displaced to the side of dehydration, in comparison with decomposition under streaming conditions. The present experiments confirm this finding. In experiment 22 the dehydrogenation was 30.5% of the total decomposition of C_3H_7OH and in experiment 24, 35%. It should be noted that the activity of different dehydrogena-

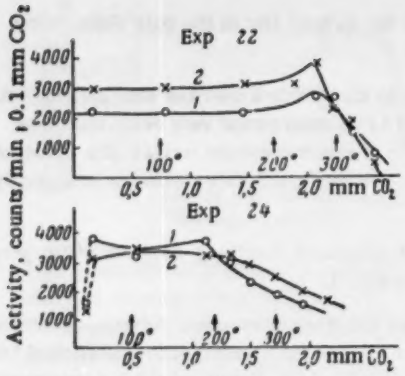

Fig. 5. Results for a differential isotopic study of the decomposition of iso-propyl alcohol on ZnO: 1) dehydrogenation; 2) dehydration. In experiment 22 inactive alcohol was adsorbed first, then active, in experiment 24 active first, then inactive.

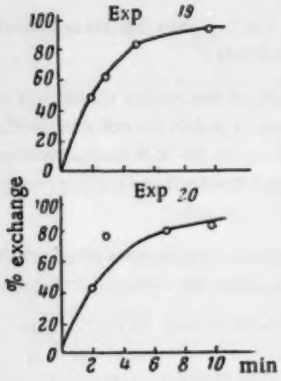

Fig. 6. Kinetics of isotopic exchange between iso-C_3H_7OH on ZnO and iso-C_3H_7OH in the bulk.

tion fractions and, similarly, of different dehydration fractions, were about the same. The mean activity of the decomposed alcohol also remained approximately constant, equal to the mean activity of the alcohol on the ZnO surface. This fact is in agreement with results of analogous experiments by Keier [2] on the decomposition of ethyl alcohol on ZnO.

Experiments on isotopic exchange on zinc oxide were carried out in the same way as for CaO and Al_2O_3. The surface coverage however was considerably higher in this case (90-100%). Results for the first ten minutes of exchange are given in Fig. 6. After this a sudden retardation in exchange was observed, and after 60 min the % exchange was practically the same as after 10 min.

The desorption and catalytic reaction in the layer of such partially exchanged alcohol was studied further, and the results of one of these experiments are given in Fig. 7.

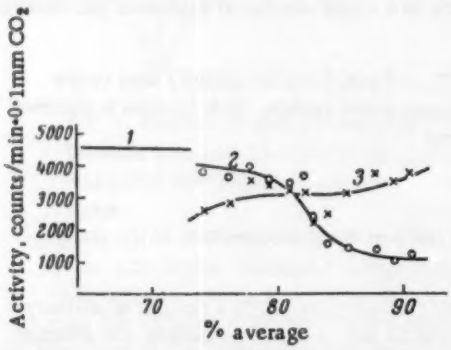

Fig. 7. Desorption (1), dehydrogenation (2) and dehydration (3) of iso-C_3H_7OH in the adsorption layer on ZnO after isotopic exchange between unmarked alcohol on the surface and marked alcohol in the bulk.

In this experiment inactive iso-propyl alcohol, adsorbed initially, underwent exchange with alcohol, marked with C^{14}, in the bulk phase. On desorption the principal quantity of alcohol (73%) came off the surface at a temperature below 90°. This alcohol was not split into fractions. Its activity was 4490 counts/min at 0.1 mm CO_2, rather higher than the average activity of the alcohol before desorption began (3990 counts/min). This is represented in the graph by a straight line. After this the activity of the dehydration and dehydrogenation fractions was determined. The first dehydrogenation fractions contained a small quantity of undecomposed alcohol.

Fig. 7 shows that the activity of the dehydrogenation products decreases continuously, i.e., in the decomposition process the catalytic dehydrogenation reaction is gradually displaced with increasing temperature to the ZnO centers, where the alcohol which does not undergo exchange occurs. On the other hand the activity of the dehydration products remains at an approximately constant level (increasing a little at the end). This level (3320 counts/min on average) is a little lower than the level of the activity of all the adsorbed alcohol (3990 counts/min), and higher than the activity of the alcohol remaining on the surface after desorption of undecomposed alcohol (2640 counts/min).

On zinc oxide the catalytic reaction proceeds on a considerably larger fraction of the total surface (20-25%) than on aluminum oxide (4-6%) and calcium oxide (2-3%).

We must point out one difference in the results for zinc oxide and aluminum oxide. On aluminum oxide the principal amount of adsorbed alcohol is decomposed in a relatively narrow temperature range (180-200°), and only quite a small fraction of alcohol, held stably to the surface, is decomposed at higher temperatures 250-350° and above (see Fig. 4). At these temperatures a cracking reaction also occurs together with dehydration. On zinc oxide both dehydrogenation and dehydration proceed over a wide temperature range (80-350°) in accordance with the wide desorption activation energy distribution. Calcium oxide occupies an intermediate position; although dehydrogenation proceeds preferentially at 180-220° and dehydration preferentially at 300-400°, considerable quantities of dehydrogenation and dehydration products are also detected during desorption at other temperatures.

This investigation therefore reveals a discrete heterogeneity of the active surface of oxide catalysts in relation to decomposition of iso-propyl alcohol. During the differential isotopic investigation of these surfaces this heterogeneity is not apparent, probably because of low activation energies. In the isotopic exchange study it appeared that the catalytic reaction proceeds on centers with high activation energies of isotopic exchange. Catalytically active centers take up a small portion of the surface of acidic (Al_2O_3) and basic (CaO) catalysts and a considerable portion of the surface (20-30%) of the semiconductor catalyst ZnO. Catalytically active sites have a certain activation energy distribution, which is wider in the case of zinc oxide.

SUMMARY

1. The distribution of active centers for the decomposition of iso-propyl alcohol on the surface of aluminum and zinc oxides, has been studied by the differential isotopic method and the method of isotopic exchange with subsequent desorption.

2. In the differential isotopic study on aluminum oxide, a constant specific radioactivity was observed for all the desorbed products from the decomposition of iso-propyl alcohol.

3. In the differential isotopic study on zinc oxide, it was observed that both the dehydrogenation products and the dehydration products of the alcohol had constant specific activities, but these activities differed from each other.

4. Isotopic exchange of iso-propyl alcohol on ZnO and Al_2O_3 is strongly retarded, which is characteristic of a heterogeneous surface.

5. A study of the desorption of alcohol from Al_2O_3 after its partial isotopic exchange indicated "topographical" heterogeneity, which is probably linked with the microporosity of the adsorbent.

6. Dehydration of iso-propyl alcohol proceeds on a small fraction (4-6%) of the Al_2O_3 surface, and there is some distribution in activation energy of these sites.

7. Dehydrogenation and dehydration of iso-propyl alcohol proceed on a considerable fraction (20-30%) of the total surface of ZnO with a wide activation energy distribution. The dehydration centers are different from the dehydrogenation centers.

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All abbreviations of periodicals in the above bibliography are letter-by-letter transliterations of the abbreviations as given in the original Russian journal. *Some or all of this periodical literature may well be available in English translation.* A complete list of the cover-to-cover English translations appears at the back of this issue.

A SIMPLIFIED CHROMATOGRAPHIC METHOD FOR DETERMINING THE SURFACE OF ADSORBENTS AND CATALYSTS

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A simple and rapid chromatographic method for determining the surface of adsorbents and catalysts has been proposed, based on the determination of the magnitude of the retention volume of the vapor of an adsorbed substance in the range of low concentrations. A linear relationship has been established between the values of the retention volumes and the specific surfaces of solids and catalysts. The method has been checked on a large number of catalysts of different chemical character.

Chromatographic methods, with simple apparatus, can be used for the rapid determination of the surface of adsorbents and catalysts. It is therefore to be expected that these methods should be extensively applied in plant laboratories and scientific research institutes.

Existing chromatographic methods can be divided arbitrarily into two groups:

a) methods based on the use of the differential balance equation of equilibrium chromatography [1-5]; in these methods integration of the chromatographic desorption curve gives the adsorption isotherm, which can then be used to calculate the magnitude of the surface:

b) methods based on the use of the specific retention volume V_g [6-8] for the direct calculation of the surface.

The first group of methods can be used to determine the absolute magnitude of the surface and to study [4] the nature of the porosity of the adsorbent. The apparatus used in these methods, however, is much more complex than that used in the second group of methods, which have not been widely adopted because until recently they were suitable only for the measurement of relative changes in the surface and did not give absolute values.

Attempts have recently been made [6, 7] to use the value of V_g to calculate the specific surface S_g.

From the kinetic theory of gases [6, 7] it follows that

$$V_g = \frac{1}{4} v \delta \frac{h}{kT} e^{\lambda/RT} \cdot S_g, \qquad (1)$$

where v is the average velocity of the molecule $= \sqrt{\frac{8}{\pi}\frac{RT}{M}}$, m/sec; h is Planck's constant $=6.6 \cdot 10^{-27}$ erg·sec; k is the Boltzmann constant $=1.38 \cdot 10^{-16}$; λ is the heat of adsorption, cal/mole; R is the gas constant =1.98 cal/mole·°C; $\delta = e^{S/R} \cdot (\frac{\alpha}{\varkappa})$, where $e^{S/R}$ is an entropy term; $\alpha < 1$ is a coefficient which takes account of the fact that not every collision between a molecule and the surface leads to adsorption; and $\varkappa$ is the pre-exponential factor in the equation for the rate constant of the monomolecular adsorption reaction.

Equation (1) is applicable for the linear part of the isotherm. Substituting in Eq. (1) the numerical values of the constants, we obtain

$$S_g = 6 \cdot 10^8 \frac{f}{\delta} \cdot 10^{-\lambda/4.577} V_g. \quad (2)$$

The value of δ is calculated from Eq. (2) by independently measuring the surface S_g and determining V_g at two temperatures T_1 and T_2 in order to calculate the heat of adsorption λ from the equation:

$$\lambda = \frac{T_1 T_2}{T_2 - T_1} R \ln \frac{V_{g_1}}{V_{g_2}}. \quad (3)$$

After substitution of the numerical value of δ in Eq. (2), the latter can be used for absolute measurements of a surface of the same chemical character, the same adsorbate being used in all the experiments.

In an analogous method recently proposed [8] for measuring the absolute magnitude of a surface, it is necessary to measure V_g for two adsorbates belonging to the same homologous series at the same temperature.

On the basis of the familiar chromatographic linear relationship between log V_g and the number n of carbon atoms, it is possible, by graphical extrapolation, to obtain the value of $(V_0)_g$, which represents the arbitrary "retention volume" when n=0. As a result we obtain an equation, analogous to Eq. (2), which can be used to calculate the absolute value of S_g:

$$S_g = 6 \cdot 10^8 \frac{\varkappa}{\alpha} (V_0)_g. \quad (4)$$

In order to determine $\left(\frac{\varkappa}{\alpha}\right)$ it is necessary to measure S_g and $(V_0)_g$ beforehand for some adsorbent by an independent method. Thus for the absolute measurement of S_g by means of Eqs. (2) or (4), three preliminary measurements are necessary: two measurements of V_g at temperatures T_1 and T_2 and one measurement of S_g [Eq. (2)] or two measurements of V_g for two members of a homologous series at a temperature T_1 and one independent measurement of S_g [Eq. (4)].

Analysis of the physical character of the coefficients δ and λ in Eqs. (2) or (4) indicates the possibility of further simplification of the procedure for calculating the absolute value of S_g from V_g.

It is natural to assume that the value of δ should change comparatively little with the nature of the adsorbent (it has been found, for example, [7] that the values of δ for silica gel and carbon differ by not more than 20%). At the same time there is a great deal of literature data [9] indicating that the difference in the heats of physical adsorption for a given adsorbate on different adsorbents has an order of magnitude not exceeding the value of RT. If this assumption is justified, we can, by combining all the coefficients preceding V_g in Eq. (2), obtain the following simple relationship:

$$S_g = A \cdot V_g \quad (5)$$

Since there are unfortunately no literature data by means of which it might have been possible to check Eq. (5), we made an attempt to verify it experimentally.

A diagram of the simple experimental assembly is shown in Fig. 1. The catalyst or adsorbent to be measured is loaded into the column 2. When the gas flow has been set up and a stable zero line obtained, the adsorptive is introduced through the cap 5 by means of a microsyringe. The appearance of a peak maximum at the moment corresponding to V_g is recorded by a detector 3 and a suitable auxiliary instrument. In a simplified version of the apparatus the automatic recorder can be replaced by a needle galvanometer or millivoltmeter.

We determined the surface S_g for all available catalysts and adsorbents with surface magnitudes from 1 to 100 m^2/g. The values of the specific retention volumes were determined simultaneously. In order to measure the adsorption isotherms necessary for the calculation of S_g, we used the other chromatographic procedure [5], based on the integration of the chromatographic desorption curve*.

*It is convenient to use standard substances for which the magnitude of the surface S_g has been determined earlier by an independent method.

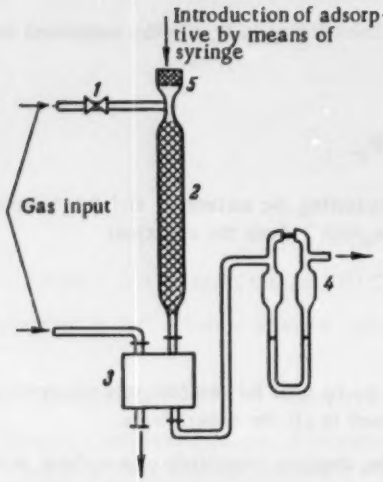

Fig. 1. Diagram of the experimental assembly for the simplified chromatographic method for determining the surface: 1) valve for the fine control of the rate of flow; 2) column with catalyst or adsorbent; 3) detector; 4) flow-meter; 5) rubber cap.

The chromatographic column was filled with a weighed quantity of the test adsorbent and a stream of carrier gas (N_2 or Ar) was passed through at a constant volume rate. Periodically, a measured quantity of adsorptive ($n\text{-}C_7H_{16}$) was injected into the column by means of a syringe and the eluate curve (Fig. 2) was recorded by means of a gas analyzer [10] placed at the outlet. The calculation from the curve was carried out as follows. The curve was broken down along its height into a number of sections n_1, n_2, etc., after which the areas S_{n_1}, S_{n_2}, etc. were determined by graphical integration. The calculation of the individual points on the isotherm was carried out by means of the equation given in [5]:

$$f(C_n) = \frac{\omega K}{ug}\int_0^n (l - l_0)\,dn = \frac{\omega K}{ug} S_n, \qquad (6)$$

where $f(C_n)$ is the quantity of substance adsorbed, mmole/g; n is the number of sections; K is the gas-analyzer constant, mmole/$/cm^3 \cdot cm$; u is the rate of movement of the automatic recorder ribbon, cm/min; ω is the volume rate of flow of the carrier gas, cm^3/min; g is the weight of the adsorbent, in grams; S_n is the area in cm^2 under the desorption curve from 0 to n_1, n_2, etc., corresponding to concentrations $C_{n_1} = Kn_1$, $C_{n_2} = Kn_2$, etc.

After construction of the isotherms from the points $f(C_{n_1})$, $f(C_{n_2})$, etc., the surface of the adsorbent was calculated by means of the BET equation.

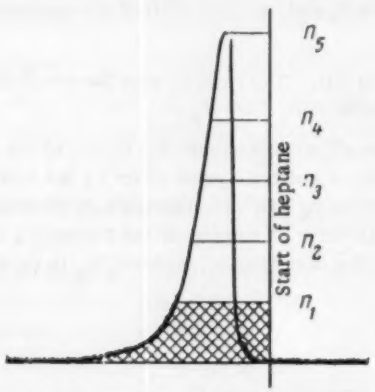

Fig. 2. A typical eluate curve recorded with an automatic recorder.

The Table and Fig. 3 (a and b) give the results obtained. These results show that, within the limits of accuracy of the measurements, Eq. (5) describes satisfactorily the experimental data for adsorbents and catalysts of extremely varied character at different rates of flow.

We thus have an extremely simple and rapid method for measuring the surface of adsorbents and catalysts. By independently determining S_g for any adsorbent with a given adsorptive we construct the graph of S_g versus V_g, after which one determination of V_g is sufficient for the calculation of the specific surface of the adsorbents under study.

When this method is used it is necessary to work in the concentration range corresponding to the linear region of the isotherms. In order to be sure that the measurements are carried out in the linear region, it is necessary to be sure that V_g is independent of the size of the specimen introduced. The size of the specimen must not be reduced too much, however, otherwise the nonuniformity of the surface may begin to have an effect.

Figure 4 shows the relationship between the retention volume V_g and the size of the specimen introduced. The figure shows that when the size of the specimen is less than 0.7 mg, V_g is constant and can therefore be used to calculate the surface from the graph (see Fig. 2). More detailed mention must also be made of the procedure for introducing the specimen during the chromatographic recording of the adsorption isotherm according to Eq. (6). When comparatively large quantities of adsorptive (up to 10 mg) are introduced in liquid form there is a peak "lag", which is apparently related to the kinetics of evaporation of the liquid. These complications can be avoided by introducing the specimen either in vapor form or into a special small-volume evaporator fitted in the upper part of the column (see Fig. 1). Figure 5 shows good agreement between the desorption branches for different sizes of specimen introduced.

Experimental Verification of Eq. (5)

Specimen	Carrier gas velocity, cm^3/min	Wt. of specimen, g	Elution time of peak, min	Retention volume V_g, cm^3/g	Magnitude of surface S_g, m^2/g
Silit	11	11	2.8	2.8	1.3
Corundum	11	10.95	2.8	2.8	1.2
Iron catalyst 1	12	3.9	2.3	7.2	2.5
Iron catalyst 2	17	8.5	3.3	6.7	2.5
ZnO phosphor	27	4.58	2.2	12.8	5.0
Sulfonated coal	14	5	3.8	10.7	4.8
ZnO + 6.2% Na_2O	31	8.05	2.2	8.4	3.4
ZnO + 0.38% Na_2O	35	7.19	2.9	11.4	4.3
ZnO + 6% ThO_2	33	3.46	1.8	17.4	7.9
ZnO + 2% $ZnSO_4$	33	5.42	3.3	20.3	8.5
Pumice	11	4.06	5.5	14.9	6.5
Ammonia catalyst 11-58	55	2.11	1.7	43.5	17.2
Spherical carrier	17	4.36	4.3	16.9	6.4
Ammonia catalyst 16-57	55	7.33	2.8	21.3	7.8
Refractory brick	90	2	2.2	100	35.4
Ni-catalyst	25	1.72	4.7	68	25.7
ZnO (ignited at 500°)	16	7.1	2.2	4.9	2.1
Iron from the oxide reduced at 480°	20	1.93	1.3	13.8	5.2
Iron from the oxide reduced at 600°	20	1.83	1.0	10.9	4.8
Shumilov iron	20	2.55	1.1	8.5	3.4
Carbonyl iron	32	6.4	1.1	5.4	2.0
ThO_2 ignited at 400°	55	1.93	0.9	26.2	10.5
ThO_2 ignited at 800°	28	2.4	0.8	9.7	4.5
White soot	42	0.28	1.7	254	100

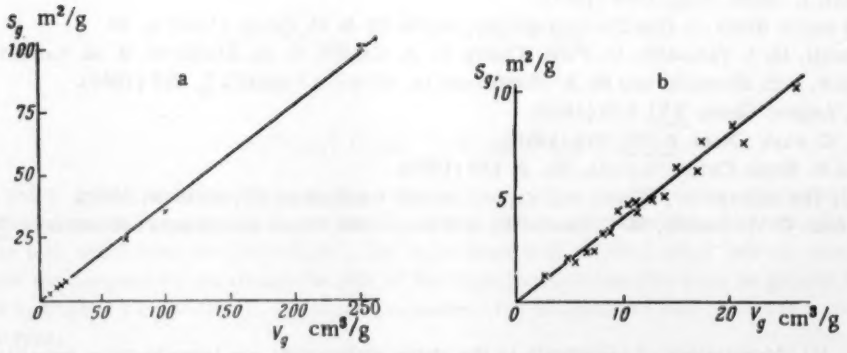

Fig. 3. Relationship between the magnitude of the surface S_g of different adsorbents and catalysts and the magnitude of the specific retention volumes, determined with n-heptane: a) from 0 to 100 m^2/g; b) from 0 to 10 m^2/g.

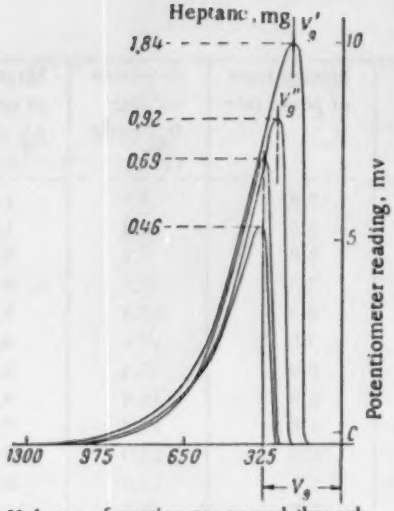

Fig. 4. Relationship between the specific retention volume V_g and the size of the liquid specimen introduced: adsorbent: silica gel (g = 1.3 g); adsorbate: n-heptane.

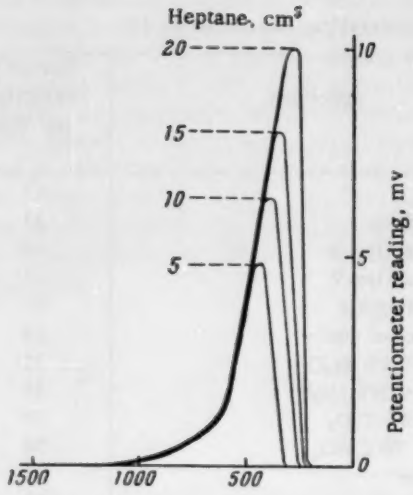

Fig. 5. Relationship between the shape of the development curve and the size of the gaseous specimen introduced: adsorbent: brick (g = 5 g); adsorbate: n-heptane; W_{N_2} = 70 cm³/min.

It cannot as yet be said that themethod is universally applicable. Complications can apparently arise, in particular, in the determination of the surface of finely porous solids, adsorbents with blind pores, etc. The exceptional simplicity of the method, however, means that it can be extensively used in those branches of science and technology where speed of measurement is important, for example in the rapid determination of the change in surface of a catalyst during its operation, the poisoning of an adsorbent with time, etc.

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THE PROBLEM OF THE NATURE OF THE TEMPERATURE MAXIMUM OF THE RATE OF HYDROGENATION OF ETHYLENE BY METALS

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On the basis of measurements of the orders of the hydrogenation reaction of ethylene by platinum and palladium metal at 100°-300°, and a comparison of the rate of the hydrogenation reaction with the rate of exchange of hydrogen with deuterium, with and without ethylene, the conclusion is drawn that in the case of platinum the temperature maximum of the rate of reaction can be explained by competition between the reactions of hydrogenation and ethylene exchange. In the case of palladium the maximum has a different nature and is evidently due to the desorption of ethylene from the surface of the catalyst at high temperatures.

It is well known that the temperature relation of the rate of the hydrogenation reaction of olefins by metals has an optimum character. At low temperatures the activation energy of this reaction is positive, at high temperatures the reaction rate decreases with an increase in temperature and the activation energy is negative. This phenomenon has been most closely investigated in the case of the hydrogenation of ethylene by nickel. Schwab and Zorn [1] suggested that the existence of a maximum is due to the fact that at high temperature desorption of ethylene takes place at the surface of the catalyst. On the other hand, Jenkins and Rideal [2] associate the temperature maximum with the desorption of hydrogen from the surface of the catalyst under these conditions. Twigg [3] suggested that the hydrogenation reaction takes place via the so-called semihydrogenated state:

$$C_2H_4\,ads + H_2 \overset{1}{\rightleftarrows} C_2H_5\,ads + H\,ads \overset{2}{\longrightarrow} C_2H_6$$

or

$$C_2H_4\,ads + H\,ads \overset{1'}{\rightleftarrows} C_2H_5\,ads + H\,ads \overset{2'}{\longrightarrow} C_2H_6.$$

Reactions 1 and 1' are reversible and lead to the exchange of ethylene when it reacts with deuterium. In Twigg's opinion, the temperature maximum is due to the fact that at high temperature the equilibria of 1 and 1' are displaced to the left, which leads to a reduction in the concentration of adsorbed ethyl radicals. According to this system, below the temperature maximum the rate of the hydrogenation reaction must be greater than the rate of exchange of hydrogen by deuterium in ethylene, while above the temperature maximum the reverse relationship must be observed.

In the above-mentioned reports, conclusions regarding the reaction mechanism were made on the basis of data on the order of the hydrogenation reaction at temperatures above and below the temperature of the optimum. However, reliable kinetic data in a wide temperature range are only available for one nickel catalyst. For this reason we investigated the kinetics and temperature relation of the rate of the hydrogenation reaction of ethylene

by other metals, namely platinum and palladium. In addition, experiments were carried out with exchange of hydrogen by deuterium, and an investigation was made of the influence of ethylene on the rate of isotopic exchange of hydrogen with deuterium according to the reaction

$$H_2 + D_2 \rightleftarrows 2HD$$

using the same samples of catalysts.

EXPERIMENTAL

The experiments were carried out in an evacuated apparatus, a diagram of which is given in Fig. 1.

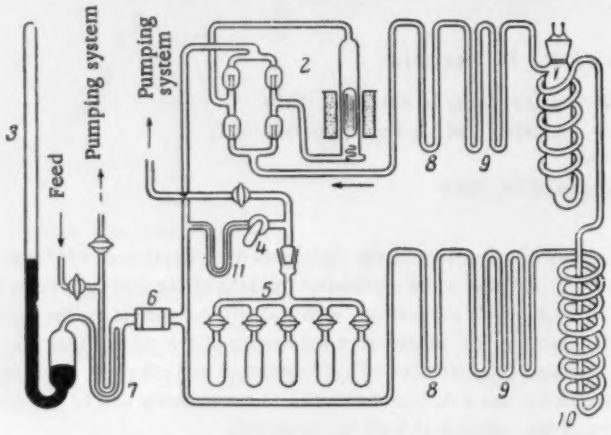

Fig. 1. Diagram of the apparatus: 1) reactor; 2) circulating pump; 3) gauge; 4) tap for taking samples for mass-spectrometric analysis; 5) "pig" with samples for mass-spectrometric analysis; 6) mercury trap; 7-11) traps cooled to -116°.

The catalyst, in the form of wire (d = 0.1, length 66 cm) when platinum was used, and foil in the case of palladium (S = 2 cm^2), was located in the reactor 1. For platinum, the temperature of the catalyst was measured by a thermocouple. The reactor was placed in the furnace. The reacting gases were mixed by a glass circulating pump 2. The pressure in the reaction zone was measured by a mercury gauge 3.

The traps 7-11, cooled by ethyl ether at its freezing point (-116°), were used to protect the catalyst from the vapor of the lubricant and mercury. Complete freezing of the catalytic poisons was achieved during this process because a further increase in the surface of the traps and a reduction in the temperature of the cooling mixture did not cause an increase in the rate of the reaction. Tap 4 was used to take samples for mass-spectrometric analysis. The volume of the apparatus was 750 cm^3.

The rate of the hydrogenation reaction was assessed from the pressure fall in the reaction zone. The rate of isotopic exchange of hydrogen with deuterium was determined mass spectrometrically, using an MS-4 apparatus. For this purpose, during the course of the reaction samples were taken in the ampoules of the "pig" 5, which was then transferred to the mass spectrometer. The mass-spectra were determined at an ionizing potential of 40 v. The rate of exchange of hydrogen by deuterium in ethylene was determined from the dilution of the initial deuterium with hydrogen.

The gases used in the experiments were prepared as follows:

Ethylene was prepared by catalytic dehydrogenation of ethyl alcohol by activated aluminum oxide. Mass-spectrometric analysis showed that this product contained 0.5% butylene and 0.5% ethane. Hydrogen and deuterium were obtained by electrolysis. Before they were introduced into the apparatus, these gases were purified from oxygen and water by passing them through a tube containing red-hot copper, and then through a series of traps cooled by liquid nitrogen.

To obtain a high activity of the catalyst and good reproducibility of the results, before each series of experiments the following standard treatment of the catalyst was employed.

The platinum wire was heated in air at 400° for 20-30 min, then in hydrogen (also for 20-30 min, at 400°) and, finally, in ethylene (30 min at 200°). After such treatment the catalyst was heated for 30 min at 300° in hydrogen before each experiment.

Similar treatment was employed in the case of palladium, the only difference being that the heating of the catalyst in hydrogen before each measurement was carried out at the temperature of the experiment to allow equilibrium to be established between the hydrogen in the gas and the hydrogen dissolved in palladium.

When the reaction of hydrogen exchange with deuterium was investigated a check was made of the activity of the catalyst after each experiment by measuring the rate of the hydrogenation reaction under standard conditions. The series of experiments is considered reproducible only if the rate of hydrogenation did not vary from one experiment to another.

RESULTS OF EXPERIMENTS

The main results obtained with a platinum catalyst are given in Fig. 2.

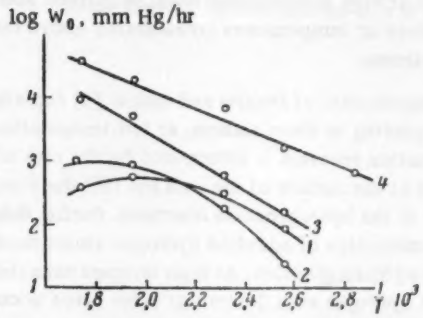

Fig. 2. Temperature relation of the activity of platinum catalyst: 1) for the initial rate of the hydrogenation reaction of ethylene; mixture with the composition (26 mm Hg ethylene + 116 mm Hg hydrogen); 2) for the initial rate of the exchange of hydrogen by deuterium in ethylene (26 mm Hg ethylene + 116 mm Hg deuterium); 3) for a doubled initial rate of exchange of hydrogen by deuterium in the presence of ethylene (26 mm Hg ethylene + 58 mm Hg deuterium + 58 mm Hg hydrogen); 4) for a doubled initial rate of exchange of hydrogen with deuterium (58 mm Hg deuterium + 58 mm Hg hydrogen).

The rate of the hydrogenation reaction of ethylene has a flat maximum at 200°. The activation energy of the hydrogenation reaction at temperatures below the temperature of the maximum is approximately 10 kcal/mole. In the temperature range investigated, ethylene reduces the rate of the reaction of the exchange of hydrogen with deuterium roughly tenfold. Here the poisoning effect of ethylene is independent of its pressure, down to very small values of the latter.

To determine the order of the hydrogenation reaction with respect to hydrogen and ethylene, we investigated the relation between the initial reaction rate and the pressure of the reagents. The results obtained for a temperature of 280°, i.e., above the temperature of the maximum, are given in Fig. 3. From the data given it is seen that at high temperature the reaction with respect to hydrogen is of the 1st order or somewhat greater. Under our experimental conditions the reaction rate is almost independent of the pressure of ethylene. According to [4], at low temperature the following relationship is observed:

$$W = k P_{H_2}^{1,3} P_{C_2H_4}^{-0,5}.$$

The principal results obtained for palladium are given in Fig. 4. The reproducibility of the results is somewhat poorer here than in the case of platinum, but within the limits of the same series of experiments the results agree fairly satisfactorily. From the data given it is seen that below the temperature of the maximum, ethylene reduces markedly the rate of the exchange reaction of hydrogen with deuterium. Above the temperature of the maximum it does not have an appreciable inhibiting effect on the rate of this reaction. The hydrogenation reaction with respect to ethylene above the temperature of the maximum of the 1st order, below the temperature of the maximum it is of zero order.

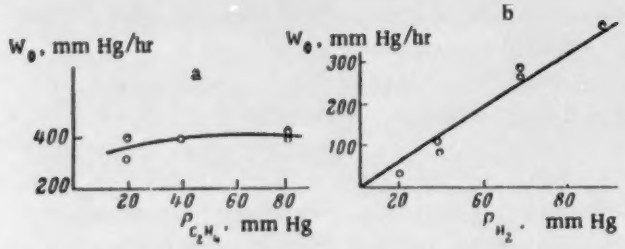

Fig. 3. Relation between the rate of hydrogenation of ethylene by platinum of 280° and the pressure of the reagents: a) pressure of hydrogen 117 mm Hg; b) pressure of ethylene 39 mm Hg.

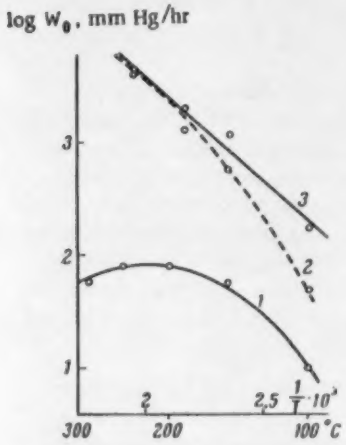

Fig. 4. Temperature relation of the activity of palladium catalyst: 1) for the initial rate of the hydrogenation reaction of ethylene (26 mm Hg ethylene + 117 mm Hg hydrogen); 2) doubled initial rate of exchange of hydrogen with deuterium in the presence of ethylene (26 mm Hg ethylene + 58 mm Hg deuterium + 58 mm Hg hydrogen); 3) doubled initial rate of exchange of hydrogen with deuterium (58 mm Hg hydrogen + 58 mm Hg deuterium).

DISCUSSION OF RESULTS

The reduction in the rate of exchange of hydrogen with deuterium in the presence of ethylene is evidently due to the fact that being adsorbed on the surface of the catalyst ethylene displaces hydrogen. This effect is observed in the case of platinum catalyst both above and below the temperature of the maximum of the rate of the hydrogenation reaction, the curve of the temperature relation of the rate of exchange of hydrogen with deuterium in the presence of ethylene being without a break near the temperature of the maximum. These results, together with the zero order of the reaction with respect to ethylene, show that Schwab's explanation which relates the temperature maximum of the rate of the hydrogenation reaction to the desorption of ethylene, cannot be correct for the case of platinum at high temperatures because marked adsorption of ethylene is observed at temperatures considerably above the temperature of the maximum.

Neither can the mechanism of Jenkins and Rideal [2] explain the results we obtained. According to these authors, at low temperatures the rate of the hydrogenation reaction is determined by the rate of the dissociation of hydrogen at the surface of the catalyst (all the dissociated hydrogen takes part in the hydrogenation reaction). During this process the rate of recombination of adsorbed hydrogen atoms must be much less than the rate of hydrogenation. At high temperatures the reaction of exchange of hydrogen with deuterium takes place according to a dissociative-associative mechanism [5,6].

$$\left.\begin{array}{l} H_2 \rightleftarrows 2H_{ads} \\ D_2 \rightleftarrows 2D_{ads} \end{array}\right\} \quad H_{ads} + D_{ads} \rightleftarrows HD.$$

The doubled initial rate of this reaction must be approximately equal to the rate of recombination of the adsorbed hydrogen atoms. The data given in Fig. 2 show that at low temperatures under our experimental conditions the rate of recombination of adsorbed hydrogen atoms (curve 3) was greater than the rate of hydrogenation (curve 1). The condition for the applicability of Jenkins and Rideal's mechanism is therefore not present.

The data we obtained for platinum can evidently be best explained by the mechanism proposed by Twigg [3]. As was mentioned above, this author explains the temperature maximum of the rate of the hydrogenation reaction by competition between the hydrogenation and exchange reactions. In this case, above the temperature of the maximum the rate of exchange of hydrogen by deuterium must be greater than the rate of hydrogenation. Below the temperature of the maximum the reverse relationship must be observed. The data we obtained (Fig. 2) show that both these conditions are satisfied in the case of platinum.

The case of palladium is quite different. Here the temperature maximum can be explained by the desorption of ethylene from the surface of the catalyst at high temperatures. This follows from the fact that the inhibiting effect of ethylene on the reaction $H_2 + D_2 = 2HD$ is shown only at low temperatures (Fig. 4), and also by the primary order of the hydrogenation reaction with respect to ethylene at high temperatures.

Our results show, therefore, that the temperature optimum of the hydrogenation reaction cannot be explained by a common mechanism in the case of different metal catalysts. It may be due to different factors in each individual case.

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KINETICS OF THE DEHYDRATION OF ALCOHOLS BY TUNGSTEN OXIDE AND THE ENERGY OF THE CARBON, HYDROGEN AND OXYGEN BONDS WITH THE CATALYST

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The kinetics of dehydration reactions of alcohols: ethyl, isopropyl, N-butyl, tertiary butyl and cyclohexanol, and the dehydrogenation of methyl alcohol and tetralin by tungsten oxide W_2O_5 were investigated under isothermal conditions. The apparent activation energies of the above-mentioned reactions and the true activation energies of isopropyl and N-butyl alcohols were determined, together with the molecular bond energies of the C, H and O atoms reacting with the catalytically active part of the surface of W_2O_5; the relation between these values and the structure of the alcohol was shown.

Dehydration of alcohols by metal oxides plays an important role in catalysis. This reaction is frequently a model reaction for studying their catalytic properties. However, with the exception of aluminum oxide [1-5] the kinetics of the dehydration of alcohols by oxides have been little studied.

In the present work the kinetics of the dehydration reaction of various alcohols were investigated, together with the dehydrogenation of methyl alcohol and tetraline under isothermal conditions [6] by W_2O_5, a very selective dehydration catalyst, widely employed in industry.

Method of Preparing the Catalyst, and the Experimental Procedure

The catalyst, blue tungsten oxide W_2O_5, was prepared in two stages. First, yellow tungsten oxide WO_3 was obtained by baking tungstic acid for 5-6 hours at 350-450° in a current of air. WO_3 was then reduced during the reaction with alcohol to W_2O_5 at the temperature of the experiment (200-390°).

The experiments were carried out in an ordinary flow apparatus with automatic feed of the initial liquid substances. The reactor was a quartz tube with a pocket for the thermocouple. The feed of gases and the collection of the gaseous products were carried out by means of a Patrikeev automatic gas tank. To simplify the kinetic calculations the experiments were carried out at low conversion percentages (not more than 30%) in the kinetic region. The gaseous catalyzate was analyzed on a VTI apparatus and by the chromatographic method. The amount of dissolved unsaturated hydrocarbons in the liquid catalyst was determined by the Kaufman-Gal'pern method [7]. The gaseous dehydration products of alcohols contained up to 98% of the corresponding unsaturated hydrocarbons, a considerable amount of them being dissolved in the liquid catalyzate. In the case of the dehydration of N-butyl alcohol the butylene content in the liquid catalyzate was about 71%. In the dehydration of ethyl alcohol the amount of dissolved ethylene could be neglected because of the low solubility of the latter. In the dehydration of primary alcohols, ethers were found in the catalyzate. The investigation was carried out at higher temperatures when a considerable amount of ethers was formed. After careful purification the initial substances had constants which agreed with literature data.

Influence of the Thermal Effect of the Dehydration Reaction

Thermal effects of the reaction have a great influence on heterogeneous-catalytic processes, particularly when catalytic reactions are carried out on industrial scale [8-12].

In experimental work, particularly during the investigation of reaction kinetics, it is extremely important to take into account the presence in the reaction zone of a radial and axial temperature gradient, caused by the thermal effect of the reaction. The axial temperature drop is generally the greatest [13, 14]. Depending on the position of the thermocouple along the length of the layer of catalyst, the measured temperature of the reaction zone may, therefore, differ markedly from the mean reaction temperature; this leads to loss of accuracy of the experimental data and even to quite incorrect results (for example, it may be found that the degree of conversion is greater than the equilibrium value). There are few references [14-17] to these problems in the literature.

When an endothermic dehydration reaction of alcohols takes place a marked rise in the temperature of the W_2O_5 catalyzate occurs which is different in different parts of the layer. Thus, different values of the activation energy will be obtained when the calculation is made, in relation to the position along the length of the catalyst layer of the junction of the thermocouple measuring the temperature. Moreover, even if the position of the thermocouple is constant the values of the activation energy of dehydration of the same alcohol, determined at different (but constant for each series of experiments) activities of the catalyst, will nevertheless differ because the temperature gradient along the length of the layer varies with a variation in the activity. In addition, strictly constant location of the thermocouple with respect to the layer becomes of great importance in the case of a high temperature drop with a short length of the catalyst layer. In actual fact, the values of the activation energy of the dehydration of the same alcohol, determined several times at different positions of the thermocouple, differed sometimes by more than 2 kcal/mole.

To determine the influence of the thermal effect of a reaction on the kinetic data, an investigation was made of the dehydration of N-butyl alcohol by 3 g of tungstic oxide (length of the layer 1.5 cm, bulk density 1.0 g/cm^3). Systematic temperature measurements carried out for four points of the layer at a distance of 0, 0.5, 1.0 and 1.5 cm from the beginning of the layer showed that dehydration of n-butyl alcohol is accompanied by a reduction in the temperature of the catalyst, this reduction being different for each section. A particularly large reduction (by 21.7° at 275°C) is observed in the initial part of the catalysts, 0.5 cm thick, while at the end of the layer there is hardly any reduction. The temperature drop increases with an increase in the temperature of the reactor heating the area. If follows, therefore, that it is often unnecessary to use a very large amount of catalyst layer, for example 5-10 cm in our case, because the initial amounts (0.5-1 cm) are sufficient to deal with the maximum load encountered and the proportion of substance converted in the subsequent sections of the catalyst is small. The presence of a high temperature gradient evidently makes it impossible to calculate the activation energy by the ordinary method. In actual fact, not one of the temperatures noted along the length of the catalyst layer can be used for plotting curves within the coordinates log $\underline{m}$ and $1/T$, where T is the temperature of the given section of the catalyst and $\underline{m}$ is the amount of substance converted in unit time (in our case, ml/min of butylene) in all sections of the catalyst layer, at different temperatures. The calculated values of the activation energies will differ according to the point of the catalyst layer at which the temperature is measured. The apparent activation energies of the dehydration of n-butyl alcohol by tungstic oxide, calculated for the four above-indicated points of temperature measurement, were 21.5, 28.0, 21.9 and 18.1 kcal/mole respectively (Table 1); as was shown by subsequent experiments, not one of the values of the activation energy obtained in this way corresponded to the true value. It follows, therefore, that the reaction must be carried out under isothermal conditions, i.e., throughout the experiment the temperature must be the same for the whole layer of catalyst and differ only slightly from the temperature of the surrounding area.

Isothermal conditions for a heterogeneous-catalytic reaction can be established by two methods, increasing the heat transfer of the system; dilution of the catalyst by an inactive substance or dilution of the initial substrate by an inert substance or the reaction products. Both methods were used simultaneously in the present work.

The catalyst (2 parts) was "diluted" with lumps of quartz (3 parts), the size of which corresponded to the size of the catalyst particles. The alcohol was diluted with the reaction product, water. The value of the adsorption coefficient of water with respect to the adsorption coefficient of n-butyl alcohol on tungstic oxide is, as indicated below, 0.56, and in the temperature range investigated is independent of temperature. In the case of alcohol-water mixtures containing comparatively little water, retardation of the reaction by adsorption of water can, therefore, be neglected.

Three aqueous solutions with molar contents of alcohol of 80, 65 and 54% were prepared. This dilution of the catalyst and alcohol ensured that in practice the process was isothermal. In this case the thermocouple was located deep in the catalyst layer, 0.5 cm from the beginning of the latter. The apparent activation energies were determined for each mixture, the values obtained being practically the same, 30 kcal/mole. The apparent activation energies of the dehydration of alcohols: ethyl, isopropyl, tertiary butyl and cyclohexanol were determined by the same method under isothermal conditions. It was found that the activation energies determined under isothermal conditions (Table 2) are approximately 10 kcal/mole higher than those obtained under non-isothermal conditions. In this connection, a regular relation is obtained between the values of the apparent activation energies and the structure of the alcohol. Ethyl and n-butyl alcohols, which are primary, are dehydrated with the same activation energy, ~30 kcal/mole. The activation energy of the dehydration of a secondary alcohol (isopropyl) was ~18 kcal/mole, i.e. the difference in the activation energy of the dehydration of primary, secondary and tertiary alcohols by W_2O_5 is approximately 6 kcal/mole. The relation we obtained is similar to that obtained by Adadurov and Krainii [18], who observed during an investigation of the dehydration of alcohols by blue tungsten oxide in a flow system that a methyl group in the α-position reduces the activation energy of the dehydration of alcohol by 5.5 kcal/mole. A similar law was previously observed by Dohse during the dehydration of alcohols by bauxite under static conditions [19].

TABLE 1

Investigation of the Influence of the Thermal Effect of the Dehydration Reaction of N-Butyl Alcohol on the Observed Value of the Apparent Activation Energy (A_1 = 72 ml/min)

Distance of the thermocouple junction from the beginning of the layer of catalyst, cm.	$\epsilon_{obs.}$, kcal/mole
0	21.5
0.5	~28
1.0	21.9
1.5	18.1

Determination of the True Velocity Constants and the True Activation Energies of the Dehydration Reaction of Isopropyl and N-Butyl Alcohols

Equation (1), which follows from Balandin's general kinetic equation [20] for monomolecular heterogeneous-catalytic reactions in a current, was employed for calculating the true velocity of reactions k.

For the case of alcohol-reaction product binary mixtures this equation has the form:

$$k = (z_2 N + z_3 A_1) \ln \frac{A_1}{A_1 - m} - (z_2 + z_3 - 1)\, m, \qquad (1)$$

where A_1 is the volumetric rate of the alcohol, ml/min, converted to N.T.P. of vapor gas; N is the total amount of alcohol and reaction products in the initial mixture, ml/min, converted to N.T.P. of vapor gas; m is the volume of unsaturated hydrocarbons liberated per unit of time in the experiments with binary mixtures, ml/min; z_2 and z_3 are the relative adsorption coefficients of water and unsaturated hydrocarbons respectively (ratio between the adsorption coefficient of the reaction product and the adsorption coefficient of the initial alcohol); z_2 and z_3 were calculated by means of equation (2), which also follows from Balandin's general kinetic equation [20]:

$$z = \left(\frac{m_0}{m} - 1\right) \Big/ \left(\frac{100}{p} - 1\right), \qquad (2)$$

where m_0 is the calculated value of m for pure alcohol and p is the molar percentage of alcohol in the binary mixture.

To calculate z_2 and z_3 by equation (2), the calculated, not the experimental value of m_0 was substituted. Employing the fact that z is a constant value at a given temperature and is independent of the percentage composition of the mixture, we substitute in equation (2) the value of p_1 and the m_1 found by experiment from one mixture, and then p_2 and the corresponding m_2 for another mixture, and solving both equations jointly with respect to m_0 we obtain the following equation for calculation:

$$m_0 = \frac{1 - a}{\frac{1}{m_1} - \frac{a}{m_2}}, \quad \text{for } a = \frac{\frac{100}{p_1} - 1}{\frac{100}{p_2} - 1}. \qquad (3)$$

TABLE 2

Apparent Activation Energy of the Dehydration of Alcohols by Tungstic Oxide Under Isothermal Conditions

Alcohol	Alcohol content in the mixture, mole %	Temperature range, °C	ϵ, kcal/mole
Ethyl	65	269-303	29.8
	80	269-301	29.0
		Mean	29.4
Isopropyl	50	168-200	23.9
	65	168-199	23.7
	80	168-200	23.7
		Mean	23.8
N-Butyl	54	230-262	29.9
	65	230 262	29.5
	65	230-262	30.5
	80	230-262	29.9
		Mean	29.9
Tertiary butyl	65	92-113	17.8
Cyclohexanol	65*	180-204	21.9

*A mixture of cyclohexanol and cyclohexene was fed through.

Since the work was carried out with three mixtures of each reaction product with alcohol, three equations of type (3) could be derived, which made it possible to calculate the mean value of m_0 for each temperature.

TABLE 3

Relative Adsorption Coefficients of the Dehydration Products of N-C_4H_9OH and iso-C_3H_7OH.

$t°$,C	z_1	z_2	$t°$, C	z_1	z_2
N-Butyl alcohol			Isopropyl alcohol		
262	0,58	0,58	200	0,48	0,42
255	0,53	0,60	192	0,55	—
245	0,37	0,71	184	0,49	0,39
235	—	0,70	176	0,50	—
230	0,76	—	173	—	0,54
Mean	0,56	0,65	Mean	0,50	0,45

TABLE 4

Check of the Applicability of the Kinetic Equation (1) to the Dehydration of Alcohols

Mole % of isopropyl alcohol in the aqueous mixture	$t°$, C	m, ml/min	k, ml/min
80	194	20,1	27,2
65	194	18,1	28,2
50	194	15,0	28,0
80	181	9,9	12,1
65	181	8,8	12,3
50	181	7,3	12,0

Table 3 gives the values of the relative adsorption coefficients found in this way for n-butyl and isopropyl alcohol under isothermal conditions. It follows from Table 3 that the relative adsorption coefficients in the temperature range investigated are independent of temperature.

The validity of equation (1) for the dehydration reactions of alcohols is confirmed by the fact that when the experimental values of m, obtained at a given temperature for mixtures of different percentage composition at constant activity of the catalyst, were substituted in the equation, the calculated values of the dehydration velocity constants were practically the same (Table 4). Table 5 give the principal results of kinetic determinations for the dehydration of N-butyl and isopropyl alcohols. From the data of this Table it is seen that the true activation energy exceeds the apparent activation energy by roughly 3 kcal/mole.

TABLE 5

Dehydration of n-Butyl and Isopropyl Alcohols by Tungstic Oxide under Isothermal Conditions

Alcohol	Temperature range, °C	z_2	z_3	ϵ_{app}, kcal/mole	ϵ_{true}, kcal/mole	k_0	$\frac{\epsilon}{\lg k_0 \cdot 10^{-3}}$
n-C_4H_9OH	230-262	0.56	0.65	29.9	33.4	$1.88 \cdot 10^{15}$	2.19
Iso-C_3H_7OH	168-200	0.50	0.45	23.7	26.1	$4.29 \cdot 10^{13}$	1.91

The Orientation of Alcohols Towards the Surface of W_2O_5

The relative adsorption coefficients z are equilibrium constants of the process of adsorption displacement of the initial substance by its conversion products from the catalytically active part of the surface. In the case of the dehydration of alcohols these are processes of displacement of alcohol by water and the corresponding unsaturated hydrocarbon. Hence, by ordinary thermodynamic equations it is easy to calculate for this process the variation in the free energy ΔF, the entropy ΔS and heat constant ΔH (i.e. the heat of adsorption displacement with the opposite sign).

From the fact that the relative adsorption coefficients of water and unsaturated hydrocarbons are independent of temperature, which is observed in our case, it follows that the ΔH values corresponding to them will be zero. Since the heats of adsorption displacement of alcohol are the same (zero), the values of the differences of the heats of adsorption of alcohols must be equal to each other. Hence it follows that during dehydration the investigated alcohols of different structure are oriented in the same way towards the catalytically active part of the surface of W_2O_5, namely to mask a group of atoms $>C-C<$ which is common and constant for each alcohol, so that

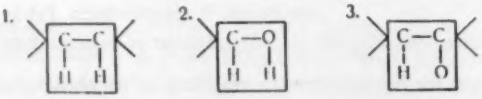
each of these atoms is bound by adsorption forces with the surface of the catalytically active points of W_2O_5.

Determination of the Bonding Energies of the C, H and O Atoms of Molecules Reacting with the Catalytically Active Surface of W_2O_5

During the process of the catalytic act itself, the adsorption bonds change; in particular their energy, characterizing the strength of the bonds, undergoes a change. If the catalytic process limits a stage of the reaction itself, a knowledge of these catalytic bonding energies is particularly necessary because they allow a conclusion to be drawn regarding the direction and order of conversion of the substance or a mixture of substances.

To calculate the bonding energies of atoms reacting with the catalytically active regions of the surface, i.e., the bonds characterizing the catalytic process, by the multiplet theory, a kinetic method for their determination has been developed [21-24].

In this method the activation energies ϵ of three different reactions are determined for the same catalyst, for example: 1) the dehydrogenation of a hydrocarbon ϵ_1; 2) dehydrogenation of an alcohol ϵ_2; 3) dehydrogenation of an alcohol ϵ_3, C, H and O atoms in different combinations (different indices) taking part in each of these reactions. Thus, for the above-mentioned reactions these indices are as follows:

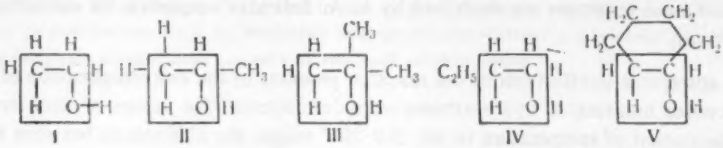


Representing the activation energy as proportional to the algebraic sum of the energies of bond breakage between the C, H and O atoms (Q_{CH}; Q_{OH}; Q_{CO}) and the bond energies of these atoms with the surface of the catalyst (Q_{H-K}; Q_{C-K}; Q_{O-K}), we obtain three equations. Solving these equations with respect to the values of Q_{HK}, Q_{CK} and Q_{OK} we obtain, after substituting the numerical values of Q_{C-H}, Q_{O-H} and Q_{C-O} taken from Kondrat'ev's data [25], the following equations:

$$Q_{H-K} = \frac{1}{3}(-\varepsilon_1 - 2\varepsilon_2 + 2\varepsilon_3) + 62;$$
$$Q_{C-K} = \frac{1}{3}(-\varepsilon_1 + 2\varepsilon_2 - 2\varepsilon_3) + 36,7; \qquad (4)$$
$$Q_{O-K} = \frac{1}{3}(3\varepsilon_1 - 2\varepsilon_2 - 2\varepsilon_3) + 48,8.$$

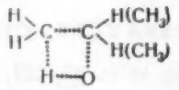
The bonding energies of C, H and O atoms, participating directly in conversions of hydrocarbon and alcohol molecules with the catalytically active part of the surface of W_2O_5, were determined in the present work by this method. For this purpose the dehydrogenation of tetralin in the 449.5-491.5 range, $\epsilon_1 = 26.8$ kcal/mole, and the dehydrogenation of methyl alcohol, $\epsilon_2 = 24.4$ kcal/mole, in the 380-420° range, were investigated using W_2O_5. To calculate Q_{H-K}, Q_{O-K} and Q_{C-K} by means of equations (4), the values of the activation energies of dehydration ϵ_3 of primary, secondary and tertiary alcohols (see Table 22) were employed, in addition to the values ϵ_1 and ϵ_2. This made it possible to study the structure of dehydrating alcohols, using the values of the bond energies.

The squares below contain the atoms of the alcohol molecule which participate directly in the dehydration reaction, being adsorbed on the active part of the surface of W_2O_5. This is a group of atoms common to all alcohols; where I is ethyl, II is isopropyl, III is tertiary butyl, IV is n-butyl and V is cyclohexanol.



As was shown above, the other radicals and atoms are not adsorbed on the catalytically active surface of W_2O_5 (these are what we may call "outside-the-square" substituents) but they influence the strength of the bonds between the atoms in the index and the strength of the bonds of each of these atoms with the catalyst.

It was found that with successive replacement of hydrogen atoms by methyl radicals at a carbon atom combined with an alcoholic hydroxyl group the values of Q_{O-K} and Q_{C-K} increase, while that of Q_{H-K} decreases (see the structure of ethyl, isopropyl and tertiary butyl alcohol in Table 6). It must be noted that both hydrogen atoms and the methyl groups which replace them do not participate directly in the reaction, i.e. the influence of the substituents "outside-the-square" on the values of the bonding energies of C, H and O with the catalyst is felt here. The variation in the values of the bond energies is due to the fact that the accumulation of methyl radicals—which weaken the C—O bond—in the alcohol leads simultaneously to a strengthening of the bond of these atoms with the surface of the W_2O_5 catalyst. The bond Q_{H-K} with the surface of the catalyst taking part in the dehydration reaction of hydrogen is weakened, probably as a result of the strengthening of the H...O bond in the intermediate multiplet complex



which runs parallel to the (C—H) axis as shown. In point of fact, in the case of substitution in ethyl alcohol of an ethyl radical for a hydrogen atom at a β-carbon atom within the index appreciable variations in the activation energies of dehydration and the bonding energies are not observed because the radical is distant from the C—O bond and has little influence on its energy (Table 6, ethyl and n-butyl alcohols). An approximately similar picture is observed when these values for cyclohexanol and isopropyl alcohol are compared. The values obtained for the activation energies and bond energies were fairly close. Thus, in the case of simultaneous displacement in ethyl alcohol of one hydrogen atom at each of two indices of carbon atoms the main influence on the value of the activation energy of dehydration and the bonding energy is exerted by substitution at the α-carbon.

SUMMARY

1. The kinetics of the dehydration of alcohols: ethyl, isopropyl, N-butyl, tertiary butyl and cyclohexanol by tungstic oxide W_2O_5 under isothermal conditions, and also the kinetics of the dehydrogenation of methyl alcohol and tetralin, were investigated.

TABLE 6

Bonding Energies of Atoms and Molecules Reacting with the Surface of W_2O_5 Catalyst

Alcohol	Activation energy of the dehydration of alcohols, ϵ_3	Values of the bond energies		
		Q_{H-K}	Q_{C-K}	Q_{O-K}
n-Butyl	29.9	56.7	24.1	39.4
Ethyl	29.4	56.4	24.5	39.7
Isopropyl	23.7	52.6	27.6	43.5
Cyclohexanol	21.9	51.5	29.5	44.6
Tertiary butyl	17.8	48.7	32.2	47.5

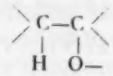
ϵ_1 - 26.6 kcal/mole, dehydrogenation of tetralin;
ϵ_2 - 24.4 kcal/mole, dehydrogenation of methyl alcohol.

2. The kinetics of these reactions are described by A. A. Balandin's equation for monomolecular heterogenous-catalytic reactions.

3. The relative adsorption coefficients of the reaction products of the dehydrogenation of alcohols, i.e., water and the corresponding unsaturated hydrocarbons, were determined. The values of these coefficients are less than unity and are independent of temperature in the 200-390° range; the differences between the heats of adsorption of the alcohol and the reaction product are, therefore, nil.

4. The true activation energies of the dehydration reaction of alcohols were determined: isopropyl 26.1 kcal/mole and butyl 33.4 kcal/mole.

5. It was concluded that dehydrating alcohols are oriented towards the surface of the catalyst by a common funtional group for all alcohols



6. The values of the bond energies of C, H and O atoms of molecules reacting with the catalytically active part of the W_2O_5 surface and the relation between these values and the structure of the alcohol was shown.

7. A method was developed for carrying out the dehydration of alcohols by W_2O_5 under isothermal conditions.

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THE KINETICS OF THE ISOTOPIC EXCHANGE OF MOLECULAR OXYGEN WITH THE OXYGEN ON THE SURFACE OF OXIDES OF IRON, COBALT, NICKEL, AND COPPER

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A study has been made of the kinetics of the exchange of the oxygen on the surface of the oxides Fe_2O_3, Co_3O_4, NiO, and CuO with molecular oxygen. The limiting stage of the exchange reaction is the adsorption of oxygen with the formation of a molecular or atomic ion. The surface of ferric oxide is uniform with respect to the exchange reaction, but the surfaces of Co_3O_4, NiO, and CuO are markedly nonuniform. The reactivities of the oxides with respect to the isotopic exchange reaction decrease in the same order as their catalytic activities with respect to the oxidation of hydrogen:

$$Co_3O_4 > NiO > CuO > Fe_2O_3 > V_2O_5.$$

The examination of the isotopic exchange of oxygen is of considerable interest in connection with the study of oxide catalysts, since it reveals the possibility of estimating the mobility and reactivity of the surface oxygen ions in oxides, the state of the adsorbed oxygen, and the degree of nonuniformity of the surface.

The isotopic exchange of oxygen with oxides has been studied by a number of authors. Cupric oxide was the first material on which isotopic exchange between oxygen and an oxide was shown to be possible, by Morita and Titani [1]. Subsequently S. M. Karpacheva and A. M. Rozen [2] confirmed that the O^{18} isotope is transferred from cupric oxide to gaseous oxygen at a temperature of 800°. Allen and Lauder [3] showed that approximately 80% of the oxygen of cupric oxide is exchanged in 4 hours at 900°. In the same work a study was made of the exchange between cobalt oxides and oxygen in the temperature range 650-880°. Detailed studies of the isotopic exchange of oxygen with oxides, particularly those of iron and nickel, were made by Winter and co-workers [4]. They established that two stages in the exchange process can be distinguished: an initial rapid stage and a subsequent slow stage. The kinetics of the rapid stage of the exchange were described satisfactorily by a first order equation, indicating the equivalence of the oxygen with respect to the isotopic exchange.

In most of the above works the kinetics of the exchange were not studied in detail and the exchange was not restricted to the surface but included a considerable fraction of the oxygen in the internal volume of the oxide.

The aim of the present study was to examine the kinetics of the surface exchange of the oxygen of the oxides Fe_2O_3, Co_3O_4, NiO, and CuO, in order to gain information on the mechanism of the process and the nature of the nonuniformity of the oxide surfaces.

EXPERIMENTAL PROCEDURE

The study of the isotopic exchange of oxygen with oxides was carried out in a static circulatory assembly (Fig. 1). The gas was circulated by means of a glass electromagnetic pump (3) [5] at a rate of 600 liter/hr. The volume of the apparatus was equal to 1 liter. Oxygen with an excess concentration of the O^{18} isotope was obtained by the electrolysis of water containing 4 at. % O^{18}, purified from traces of hydrogen on a platinum catalyst, dried in columns with solid alkali and silica gel and in a trap cooled with solid carbon dioxide, and passed to a storage flask (4). Oxygen of normal isotopic composition was prepared by the electrolysis of twice-distilled water. A weighed specimen of the oxide was placed in the reaction vessel (1), which was heated by means of a heater (2), and treated in vacuo for 8 hours at a temperature of 400° and a residual pressure of 10^{-4}-10^{-5} mm Hg. A quantity of oxygen enriched in the O^{18} isotope was measured from the pressure in the calibration volume, passed into the circulatory circuit, and the circulation was started. The oxygen pressure was measured by means of U-shaped manometers (5) and (6) filled with mercury and dibutyl phthalate and a "spoon" manometer (7) as null-indicator [6]. The start of the circulation was taken as the start of the experiment. Gas specimens were removed at intervals into an ampoule (8) and the isotopic composition analyzed with an MS-I mass spectrometer. The error in the determination of the O^{18} concentration amounted to ± 2% of the quantity being measured.

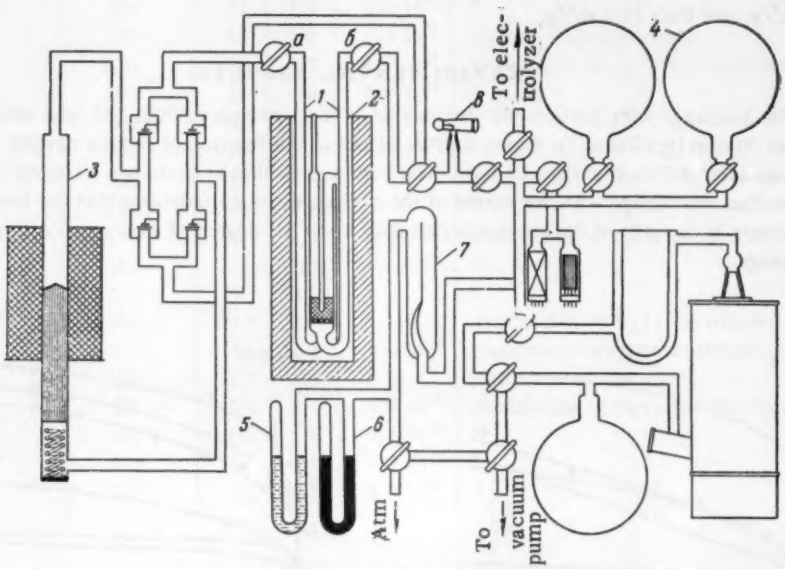

Fig. 1. Diagram of the apparatus.

Studies were made of the influence of temperature, oxygen pressure, and change in the stoichiometric composition of the oxides on the rate of exchange. The stoichiometry was altered by altering the preliminary treatment of the oxides. The lowest oxygen content was shown by specimens freshly degassed in vacuo at a temperature of 400°. Increase in the oxygen content was achieved by keeping the oxide, after degassing, for 2 hours at 400° in an atmosphere of oxygen of natural isotopic composition. Subsequent evacuation of oxygen was carried out at a temperature of 200°

The fraction of the surface oxygen ions attaining the isotopic composition of the gas phase was calculated from the experimental data according to the equation

$$x = \frac{\alpha\left[(C_0 - C_1) + (C_0 - C_2) + \ldots + (C_0 - C_{n-1})\right] + \left[1 - \sum_{1}^{n-1} \alpha\right](C_0 - C_n)}{\lambda\,(C_n - 0{,}2)}, \qquad (1)$$

where C_0 is the O^{18} concentration in the gas initially, at. %; C_n is the O^{18} concentration in the nth sample of gas,

at. %; 0.2 is the natural O^{18} concentration, at. %; $\alpha = \frac{n_{sample}}{n_g^0}$ is the sample fraction; n_{sample} is the quantity of gas in the sample removed for analysis; n_g^0 is the quantity of gas initially; and $\lambda = \frac{n_{solid}}{n_g^0}$ is the ratio of the quantities of oxygen in the surface layer of oxide and in the gas.

In the calculation of λ the ionic radius of oxygen was taken as equal to 1.4 A.

Preparation of the Oxides. Nickel monoxide was prepared by thermal decomposition of ferric hydroxide at 500° in a current of oxygen. The hydroxide was precipitated from ferric chloride solution by ammonia.

Cupric oxide was prepared by precipitation from copper sulfate and caustic soda solutions.

Cobalto-cobaltic oxide was prepared by decomposition of cobalt nitrate at a temperature of 400°.

The resultant powdered oxides were washed repeatedly with water, formed into tablets, and the tablets were broken down to a particle size of approximately 3 mm and heated in a current of oxygen for 8 hours at a temperature of 400°. The values for the specific surface of the oxides, determined by the low-temperature adsorption of nitrogen and calculated by means of the BET equation, were as follows: Co_3O_4 7.7 m^2/g; Fe_2O_3 27.2 m^2/g; NiO 7.8 m^2/g; and CuO 17.6 m^2/g.

EXPERIMENTAL RESULTS

I. Fe_2O_3. The exchange with ferric oxide was studied at temperatures of 300, 350, and 400° and oxygen pressures of 10 and 30 mm Hg (Table 1). Figure 2 gives values of the fraction of surface oxygen which has undergone exchange after different periods of time. The curves show that at exchange fractions less than 1 the rate of the process does not change with the extent of the exchange, which indicates that the ferric oxide surface is uniform. A decrease in the rate of the process begins only when the degree of exchange corresponds to more than surface exchange.

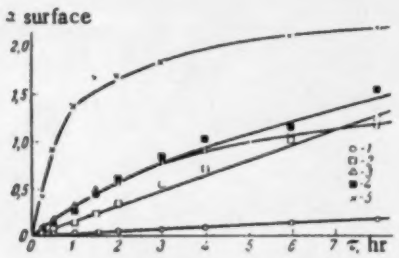

Fig. 2. Relationship between the fraction of ferric oxide surface oxygen which has undergone exchange and the duration of exchange; 1) expt. 13; 2) expt. 10; 3) expt. 11; 4) expt. 12; 5) expt. 9.

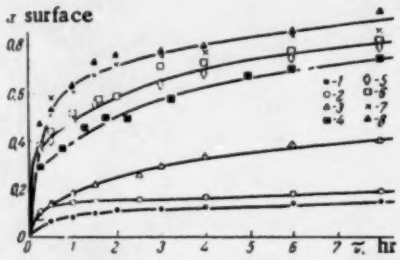

Fig. 3. Relationship between the cobalto-cobaltic oxide surface oxygen which has undergone exchange and the duration of exchange: 1) expt. 7; 2) expt. 6; 3) expt. 8 (the values of x in the Figure have been increased by a factor of 10); 4) expt. 5; 5) expt. 4; 6) expt. 3; 7) expt. 1; 8) expt. 2.

The rate of exchange at a temperature of 350° in the pressure range 10-30 mm Hg is proportional to the oxygen pressure to the power 0.8 (in Winter's experiments [4] first order was obtained).

TABLE 1

The isotopic exchange of oxygen with oxides of iron, cobalt, nickel, and copper

Oxide	Expt. No.	Expt. temp t, °C	P_{O_2}, mm Hg	λ	R_{av}, at./m^2·hr	Notes
Co_3O_4	1	300	32	0.8	$1.1 \cdot 10^{25}$	Evacuation of O_2 (after treatment) at 200°
(m = 0.7)	2	300	34	0.7	$1.2 \cdot 10^{15}$	" "
	3	300	9.5	2.8	$4.8 \cdot 10^{24}$	" "
	4	300	11.5	2.2	$5.5 \cdot 10^{24}$	Freshly degassed oxide
	5	300	10	2.5	–	Without evacuation of oxygen
	6	200	11	2.4	$7.6 \cdot 10^{22}$	Evacuation of O_2 (after treatment) at 200°
	7	200	10	2.6	–	Without evacuation of oxygen
	8	100	10.5	2.4	$1.0 \cdot 10^{20}$	Evacuation of O_2 (after treatment) at 200°
Fe_2O_3	9	400	9.5	4.9	–	" "
(m = 0.8)	10	350	10	5.5	$6.2 \cdot 10^{17}$	" "
	11	350	31	1.6	$1.6 \cdot 10^{18}$	" "
	12	350	10	5.2	$1.0 \cdot 10^{18}$	Freshly degassed oxide
	13	300	11	4.7	$1.0 \cdot 10^{17}$	Evacuation of O_2 (after treatment) at 200°
NiO	14	300	10	2.6	$6.0 \cdot 10^{20}$	" "
(m = 0)	15	300	30	0.9	$6.0 \cdot 10^{20}$	" "
	16	250	10	2.3	$1.7 \cdot 10^{20}$	" "
	17	250	10	2.3	–	Freshly degassed Oxide
	18	250	10	2.3	–	" "
	19	200	10	2.3	$3.4 \cdot 10^{19}$	Evacuation of O_2 (after treatment) at 200°
	20	150	10	2.3	$4.6 \cdot 10^{18}$	" "
CuO	21	300	30	0.6	–	" "
(m = 1)	22	250	10.2	3.7	–	Evacuation of O_2 (after treatment) at 250°
	23	250	10	2.0	$1.6 \cdot 10^{19}$	Duration of oxygen treatment 12 hr
	24	250	9.8	3.8	–	Freshly degassed oxide
	25	200	10.2	3.7	$2.0 \cdot 10^{18}$	Evacuation of O_2 (after treatment) at 200°
	26	200	30	0.6	$6.0 \cdot 10^{18}$	" "
	27	200	30	1.0	$6.0 \cdot 10^{18}$	" "
	28	172	10	3.8	$4.9 \cdot 10^{17}$	" "

The conditions of the preliminary treatment of the oxide with oxygen have little effect on the rate of exchange. Thus at 350° and P_{O_2} = 10 mm Hg the rate of exchange after treatment with oxygen was lower than that for a freshly degassed specimen by a factor of only 1.5.

The influence of temperature on the rate of exchange was studied at an oxygen pressure of 10 mm Hg and temperatures of 300, 350, and 400°. In the last case the exchange of a certain fraction of "internal" oxygen took place in addition to the exchange of "surface" oxygen, and the calculation of the activation energy was carried out from the rates of exchange at 300 and 350°.

II. Co_3O_4. The exchange of the O^{18} isotope between oxygen and cobalto-cobaltic oxide was studied in the temperature range 100-300° at oxygen pressures of 10 and 30 mm Hg (Table 1 and Fig. 3). Figure 3 shows that the rate of the exchange process decreases considerably with increase in the fraction of the atoms which have undergone exchange. Since the retardation takes place at degrees of surface exchange much less than unity, the decrease in the rate of exchange cannot be attributed to diffusion retardation and it must be assumed that the surface oxygen ions of cobalto-cobaltic oxide are not equivalent with respect to isotopic exchange.

A study was made of the relationship between the rate of exchange and the oxygen pressure at a temperature of 300°. From the reciprocals of the times taken to reach identical degrees of exchange it was found that the rate of the process is proportional to the oxygen pressure to the power 0.7.

The rate of exchange increases markedly with increase in the temperature.

In order to study the influence of change in the stoichiometric composition of the oxide on the rate of exchange, we carried out three different series of experiments:

1) exchange with oxide freshly degassed in vacuo at 400°;

2) exchange with oxide treated with oxygen after degassing in vacuo at 400°, with subsequent evacuation at 200°;

3) exchange with oxide treated with oxygen at 400° without subsequent evacuation of oxygen.

The reaction vessel was disconnected by means of the valves (a and b in Fig. 1) and the oxygen in the remaining part of the circulatory circuit was replaced by oxygen enriched in O^{18}. The reaction vessel was then reconnected, the circulation was started, and the experiment was continued in the usual way.

The rates of exchange in the first two cases were equal. In the third case a decrease in the rate relative to that in the first two cases was observed: by a factor of approximately 2.5 at 300° and by a factor of 8 at 200°.

The results of the experiments in the third series eliminate the possible suggestion that the decrease in the rate is due to a change in the degree of covering of the surface by oxygen during the course of the experiment as a result of the slow adsorption of oxygen, which might have influenced the surface properties of the oxide and been manifested as a form of "induced" nonuniformity, since retardation of the process would have been observed in this case also. The nonequivalence of the oxygen with respect to isotopic exchange must be a feature of the original oxide.

III. NiO. The isotopic exchange of oxygen with nickel oxide was studied at temperatures of 150-300° and oxygen pressures of 10 and 30 mm Hg (Table 1 and Fig. 4). At temperatures above 250° a certain fraction of "internal" oxygen is exchanged in addition to the "surface" oxygen of the oxide. It should be noted that the "fraction of exchange versus time" curves show no sharp boundary at fractions of surface exchange greater than unity.

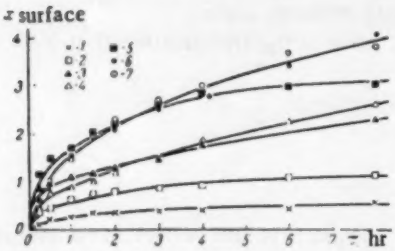

Fig. 4. Relationship between the fraction of nickel oxide surface oxygen which has undergone exchange and the duration of exchange: 1) expt. 20 (the values of x in the Figure have been increased by a factor of 10); 2) expt. 16; 3) expt. 17; 4) expt. 19 (the values of x in the Figure have been increased by a factor of 10); 5) expt. 18; 6) expt. 15 (the values of x in the Figure have been reduced by a factor of 1.5); 7) expt. 14 (the values of x in the Figure have been reduced by a factor of 1.5).

The rate of exchange decreases with increase in the the degree of exchange even when $x < 1$, which indicates that the surface is nonuniform. It was established that at 300° the rate of exchange is independent of the oxygen pressure in the range 10-30 mm Hg, in agreement with literature data [4]. The rate of exchange was characterized by the reciprocal of the time taken to attain a given degree of surface exchange. Figure 4 shows that the fraction of surface ions which have undergone exchange increases markedly with increase in temperature.

Experiments in which the preliminary treatment of the nickel oxide was varied showed that the greater the saturation with oxygen, the slower the exchange with oxygen in the gas phase.

IV. CuO. The isotopic exchange of oxygen between molecular oxygen and cupric oxide was studied at oxygen pressures of 10 and 30 mm Hg in the temperature range 172-300°. The experimental results are given in Fig. 5 and Table 1. For a freshly degassed specimen and a specimen treated with oxygen but subsequently evacuated not at 200° but at 250° the degree of exchange attained after equal intervals of time was greater than that in Expt. 23, in which the oxide was kept in an atmosphere of oxygen at 400° for 12 hours.

The rate of exchange at a temperature of 200° is directly proportional to the oxygen pressure in the gas phase.

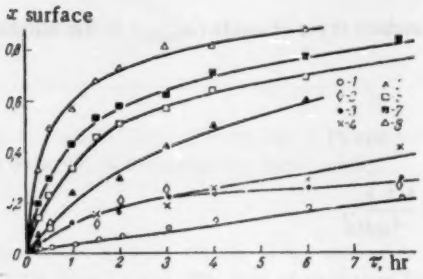

Fig. 5. Relationship between the fraction of the cupric oxide surface oxygen which has undergone exchange and the duration of exchange: 1) expt. 25; 2) expt. 26; 3) expt. 27; 4) expt. 28 (the values of x in the Figure have been increased by a factor of 10); 5) expt. 23; 6) expt. 22; 6) expt. 22; 7) expt. 24; 8) expt. 21 (the values of x in the Figure have been reduced by a factor of 1.5).

DISCUSSION OF RESULTS

The exchange of oxygen atoms between molecular oxygen and solid oxides is a complex process involving a number of successive elementary stages, for example:

$$\text{I. } O_{2\,gas} \rightleftarrows O_{2\,ads}$$
$$\text{II. } O_{2\,ads} + e \rightleftarrows O_{2\,ads}^{-}$$
$$\text{III. } O_{2\,ads}^{-} + e \rightleftarrows 2O_{ads}^{-}$$
$$\text{IV. } O_{ads}^{-} + e \rightleftarrows O^{2-}$$

It is subsequently assumed that the oxygen in the form O^{2-} is identical with the oxygen of the oxide lattice.

The assumption that the oxygen is adsorbed on the oxides in the negatively charged form is confirmed by the influence of the adsorbed oxygen on the electrical conductivity and the work of removing an electron [7].

The last step (IV), which involves the actual exchange, may take place in two ways [8]:

1) with the participation of anionic defects (lattice sites which are not occupied by oxygen) on the oxide surface. In this case the exchange is associated with the transfer of an atomic oxygen ion from the adsorbed layer into the anionic defect on the oxide surface and back again without displacement of the crystal–gas boundary. The diffusion of the anionic defects from the surface into the depth of the crystal determines the rate of isotopic exchange with oxygen inside the oxide crystal. If the diffusion of the anionic defects is much slower than their formation and filling on the surface, then the stage involving exchange with the oxygen on the surface of the oxide lattice and the stage involving exchange with the oxygen in the bulk of the crystal can be distinguished clearly:

2) as a result of electronic transitions without displacement of the oxygen ions. The conversion of an adsorbed oxygen ion to an oxygen ion of the lattice and the reverse process are accompanied in this case by a displacement of the cations in the oxide lattice, i.e. by a displacement of the crystal boundary.

Strictly speaking, for this exchange mechanism we cannot examine the exchange of oxygen on the surface and the exchange of oxygen in the bulk of the oxide separately. In the range of low degrees of exchange, however, the kinetic relationships do not differ greatly in the two cases.

Kinetics of Exchange. If the exchange is limited to the surface oxygen ions and the oxygen in the bulk of the crystal does not take part in the exchange, the rate of exchange is given by the equation:

$$-n_g \frac{dC}{d\tau} = RS(C - C_s), \qquad (2)$$

where R is the rate of exchange, atoms of oxygen/m^2·hr; n_g is the number of oxygen atoms in the gas phase; τ is the exchange time, hr; C is the O^{18} concentration in the gas, at. %; C_s is the O^{18} concentration in the surface layer of the lattice, at. %; and S is the surface area of the oxide, m^2.

When all the oxygen atoms in the surface are equally reactive, i.e. when the oxide surface is uniform with respect to exchange with oxygen, R is constant and C_s can be calculated from the balance equation:

$$C_s = \frac{1+\lambda}{\lambda} C_\infty - \frac{C}{\lambda}. \quad (3)$$

Here C_∞ is the O^{18} concentration in the surface layer when equilibrium distribution of isotopes has been reached; $\lambda = \frac{n_{solid}}{n_g}$ is the ratio of the number of oxygen atoms in the surface layer of oxide (n_{solid}) to the number of oxygen atoms in the gas phase.

Integrating Eq. (2) and using Eq. (3) we find:

$$\ln(1-F) = -RS\frac{1+\lambda}{n_{solid}}\tau, \quad (4)$$

where $F = \frac{C_g - C}{C - C_\infty}$ is the extent to which equilibrium has been approached; it is readily calculated from the isotopic composition of the gas phase.

Equation (4) is also applicable to rapid internal exchange when the isotopic composition on the surface and in the bulk of the crystal are the same during the exchange process. In this case n_{solid} in Eq. (4) should be replaced by the total number of oxygen atoms in the oxide phase.

It should be noted that when the mobility of the oxygen in the oxide lattice is high, first order kinetics may be observed even when the surface is nonuniform [9].

If exchange with the internal oxygen of the oxide does not take place and the surface is nonuniform with respect to exchange, Eq. (2) can be applied only to individual groups of surface oxygen ions with the same reactivity with respect to exchange:

$$g\frac{dC_x}{d\tau} = R(x)(C - C_x), \quad (5)$$

where R(x) is the rate of exchange for regions of the surface of a given type; g is the number of oxygen ions per 1 m^2 of surface; and C_x is the O^{18} concentration for a region of a given type.

Integration of Eq. (5) can be used to determine what should be the rate of exchange for regions of a given type in order that after time τ the isotopic composition of their oxygen should have an average value between the initial isotopic composition of the surface oxygen and the isotopic composition of the gas phase at that moment:

$$R(x) = \frac{1}{\tau}\frac{g}{\ln 2}. \quad (6)$$

All regions of the surface for which R(x) is much greater than the value given by Eq. (6) arrive after time τ at isotopic equilibrium with the gas, and all those regions for which R(x) is much less than this value retain the initial isotopic composition. Regions for which the values of R(x) are close to that given by Eq. (6) will have intermediate isotopic composition.

If the nonuniformity is considerable, the fraction of these intermediate regions will be very small and in order to calculate the extent of the exchange it is possible to use the method proposed by S. Z. Roginskii [10] for the calculation of the degree of adsorption on nonuniform surfaces. We shall make the approximate assumption that the fraction of intermediate regions is very small, i.e. that for every value of τ all the oxygen ions with $R > R(x)$ will reach isotopic equilibrium with the gas phase, while the oxygen ions with $R < R(x)$ retain the initial isotopic composition. The experimentally observed relationship between $\underline{x}$ and τ can then be used to establish the relationship between R(x) and $\underline{x}$, i.e. the nature of the nonuniformity.

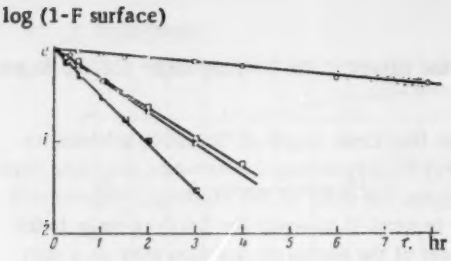

Fig. 6. Relationship between log (1-F) and the duration of exchange for ferric oxide.

Examination of the above experimental data shows that the exchange on ferric oxide is described satisfactorily by Eq. (4), indicating that the surface oxygen ions of this oxide are uniform (Fig. 6).

In this part our results agree with Winter's data [4].

The kinetics of the isotopic exchange of oxygen between gaseous oxygen and the surface oxygen ions of the oxides of nickel, cobalt, and copper do not obey the first order equation, indicating that the surface oxygen of these is nonuniform with respect to isotopic exchange, although in [4] it was assumed that the surface of nickel monoxide is uniform.

Let us assume that the change in the rate of exchange for different regions of the surface is related to a change in activation energy. The rate of exchange for a given fraction of the surface exchange is:

$$R(x) = k_0 e^{-\frac{E(x)}{RT}} P_{O_2}^m, \quad (7)$$

where k_0 is a constant, E(x) is the activation energy of exchange for a given degree of exchange x; and $P_{O_2}^m$ is a factor characterizing the relationship between the rate and the oxygen pressure.

By means of Eq. (7) it is possible to calculate the change in the activation energy of exchange for a fraction of the surface, characterized by the redistribution function:

$$\rho(E) \quad \frac{dx}{dE}. \quad (8)$$

Examination of the experimental data shows that the exchange isotherms for the oxides of cobalt, nickel, and copper show the closest correspondence to straight lines when the coordinates used are log x versus log τ, corresponding to the exponential distribution:

$$\rho(E) \quad He^{\alpha E}. \quad (9)$$

The values of the constants in Eq. (9) are given in Table 2.

TABLE 2

Constants of Eq. (9) and values of the initial $R_{init.}$ and average $R_{av.}$ rates of exchange at 200° and an O_2 pressure of 10 mm Hg

Oxide	k_0	α	H	$R_{init.}$, at./$m^2 \cdot hr$	$R_{av.}$, at./$m^2 \cdot hr$
Co_3O_4	$1.02 \cdot 10^{34}$	$1.66 \cdot 10^{-4}$	$9.11 \cdot 10^{-8}$	$4.3 \cdot 10^{23}$	$7.2 \cdot 10^{22}$
NiO	$7.52 \cdot 10^{29}$	$4.85 \cdot 10^{-4}$	$4.61 \cdot 10^{-10}$	$6.8 \cdot 10^{21}$	$3.4 \cdot 10^{19}$
CuO	$2.33 \cdot 10^{30}$	$5.92 \cdot 10^{-4}$	$2.82 \cdot 10^{-12}$	$6.3 \cdot 10^{21}$	$2.0 \cdot 10^{18}$
Fe_2O_3	–	–	–	$8.7 \cdot 10^{14}$*	$8.7 \cdot 10^{14}$

*Obtained by extrapolation.

The change in the activation energy of exchange along the surface (Fig. 7) can be used to compare the nonuniformity of the surfaces of different oxides. The greatest nonuniformity is observed for cobalto-cobaltic oxide; nickel and copper oxides show less nonuniformity, and the surface of ferric oxide is uniform.

It is important to note that nonuniformity appears in oxides containing ions of different charge. It is possible that the cause of the nonuniformity is the difference in the positions of oxygen ions relative to cations of different valences. Changes in the stoichiometric composition of copper and nickel oxides lead to the appearance of cations with a different valence, and this can lead to nonuniformity of the surface [11].

The order of the reaction with respect to oxygen depends on the nature of the limiting stage and the degree of covering of the surface by adsorbed oxygen.

If the rate of exchange is determined by the rate of one of the first three stages of the above scheme, in which molecular oxygen takes part, the order of reaction with respect to oxygen may lie between unity and zero. For a low degree of covering of the oxide surface with adsorbed oxygen, the order of the exchange reaction will be close to unity and for a high degree of covering it will be close to zero. If however the limiting stage is the fourth stage in which only the atomic oxygen ion takes part, the order of the exchange reaction may vary only between one half and zero.

The experimentally observed relationships between the rate of exchange and the oxygen pressure (Table 1) lead to the conclusion that for the oxides of iron ($m = 0.8$), cobalt ($m = 0.7$), and copper ($m = 1$), stage IV cannot be the limiting stage. In the case of ferric oxide this conclusion agrees with the result obtained by Winter, who found that for iron and nickel oxides the rates and activation energies for the exchange of the oxygen of the oxide and the homomolecular exchange of oxygen ($O_2^{16} + O_2^{18} \rightarrow 2O^{16}O^{18}$) coincide.

It is natural to assume that the exchange in molecular oxygen involves only the first three stages of the general scheme so that only one of these stages can be the common limiting stage for the two reactions.

In the case of nickel monoxide, no conclusions regarding the nature of the limiting stage can be reached from the magnitude of the order of the reaction. The above data given by Winter suggest that for this oxide also, the limiting stage is one of the first three stages.

The data on the influence of the preliminary conditions and treatment of the oxides with oxygen indicate that the limiting stage is associated with the electron transfer between the oxide and adsorbed oxygen. For the oxides of cobalt, nickel, and copper, the rate of exchange increases appreciably when part of the oxygen is removed by treatment at high temperatures and decreases after preliminary treatment with oxygen. This is apparently due to a change in the stoichiometric composition of the oxide layer next to the surface, which leads to a change in its electronic structure and in the position of the chemical potential level. The displacement of the chemical potential level cannot influence the rate of stage I, which is not associated with electronic transitions, and should have a significant influence on the rate of stages II and III, as a result of the change in the adsorption equilibrium of oxygen in the forms O^{2-} and O^- and as a result of the change in the activation energy.

Analogous results were obtained by Winter [4a], who found an increase in the rate of the isotopic exchange of oxygen with some oxides with increase in the duration of the degassing treatment or with increase in the temperature of the vacuum treatment.

If the adsorption coefficients change only as a result of the displacement of the chemical potential level [12] and the direction of the change in the activation energy is opposite to that of the change in heat of adsorption (antibathic relationship) [13], of the change in heat of adsorption (antibatic relationship) [13], then when the chemical potential level changes by $\Delta\varphi$ the rates of reaction towards the right (the adsorption stage) decrease: for stage II by a factor of $e^{\alpha\Delta\varphi/RT}$ for any degree of covering of the surface by oxygen and for stage III by a factor of $e^{(1+\alpha)\Delta\varphi/RT}$ in the range of low degrees of covering and by a factor of $e^{\alpha\Delta\varphi/RT}$ in the range of high degrees of covering of the surface by adsorbed oxygen. The rates of the reverse reactions (the desorption stages) decrease at low degrees of covering: by a factor of $e^{\alpha\Delta\varphi/RT}$ for stage II and by a factor of $e^{(1+\alpha)\Delta\varphi/RT}$ for stage III. In the range of high degrees of covering, on the other hand, they increase by a factor of $e^{(1-\alpha)\Delta\varphi/RT}$.

In the case of exchange with the oxides of cobalt, iron and copper, the process takes place at low degrees of covering and in every case decrease in the chemical potential level should lead to a decrease in the rate of exchange.

All this indicates that in the isotopic exchange of oxygen with the oxides of cobalt and copper the limiting stage is the adsorption of oxygen with the formation of a molecular or atomic ion.

It is probable that the nature of the limiting stage is the same for the exchange with the oxides of iron and nickel.

In order to compare the tendency of the different oxides to undergo isotopic exchange with oxygen, we calculated the initial and average rates of exchange for a temperature of 200° and an oxygen pressure of 10 mm Hg (Table 2). In both cases the comparison leads to the following sequence:

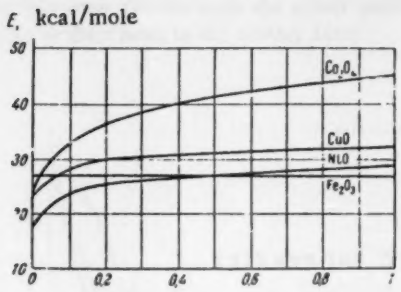

Fig. 7. Change in the activation energy of exchange along the surface.

$$R_{Co_3O_4} > R_{NiO} > R_{CuO} > R_{Fe_2O_3} > R_{V_2O_5}{}^{*}.$$

An interesting feature is that this sequence agrees, on the whole, with that found earlier for the decrease in the catalytic activity of the oxides with respect to the oxidation of hydrogen [14].

The rates of both the isotopic exchange and the oxidation of hydrogen are apparently determined by the adsorbed oxygen concentration, which varies for the different oxides in the above sequence.

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All abbreviations of periodicals in the above bibliography are letter-by-letter transliterations of the abbreviations as given in the original Russian journal. *Some or all of this periodical literature may well be available in English translation.* A complete list of the cover-to-cover English translations appears at the back of this issue.

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* Rate calculated from the data given in [9].

ON THE EFFECT OF COPPER ON THE CATALYTIC PROPERTIES OF SKELETAL NICKEL CATALYST

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November-December, 1960
Original article submitted February 20, 1960

The causes of the decrease in the catalytic activity, magnetic susceptibility, and surface area of catalysts formed by dissolving the Al out of Al–Ni–Cu alloys, which accompanies an increase in their copper content, were studied in this work. On the basis of x-ray structural investigations, study of phase diagrams, and phase-solubility measurements it is shown that the change in the above-indicated properties is due to a decrease in the quantity of active ("skeletal") nickel formed, resulting from a change in the phase composition of the ternary alloy and the solubility of the phases.

Data on the effect of adding a series of transition metals to Al–Ni alloy and subsequently dissolving out the aluminum on the properties of the resulting "skeletal" nickel catalysts are given in [1]. The catalysts obtained have extremely high, but approximately identical, specific activities in the benzene hydrogenation reaction. This is due, as it turned out, to the fact that the indicated metals (Cr, Ti, V, Mo, Co) do not form solid solutions to any appreciable degree with the metallic nickel left when the aluminum is dissolved out, and hence the electronic structure of the nickel is not changed.

According to concepts developed by Dowden [2] et al., addition to nickel of metals in Group Ib of the Periodic System should cause filling of the d-zone of the nickel and should lead to a decrease of catalytic activity in hydrogenation reactions, and of magnetic susceptibility. Actually, a number of authors [3-7] showed that the addition of copper, silver, or gold to nickel, platinum, palladium, etc., causes a sharp change in their properties: The magnetic susceptibility decreases, the Curie point falls, and the degree of hydrogen adsorption and catalytic activity diminish in a number of reactions. In particular, Reynolds [3] and Cratty and Russell [4] studied the catalytic properties of nickel-copper catalysts in comparison with their magnetic and other properties.

Reynolds studied two types of catalysts, prepared by: a) coprecipitation on Kieselguhr of nickel and cupric oxides from their salts with subsequent reduction to the metals, and b) dissolving the Al out of Al–Ni–Cu alloys (50% Al)–"skeletal" catalysts.

It has been shown several times by the x-ray method [4, 8] that in the coprecipitation of oxides and reduction to the metals, true alloys of these metals are obtained which do not differ in phase composition from the alloys obtained by ordinary fusion.

For coprecipitated catalysts Reynolds obtained curves of the relation between the magnetic susceptibility and activity of coprecipitated catalysts and their composition (Fig. 1) and came to the conclusion, in agreement with Dowden's concept, that the decrease of catalytic activity on increase of the copper content in the nickel-copper solid solution, is caused by filling of the nickel d-zone by electrons of the copper. Reynolds then obtained qualitatively analogous relations for "skeletal" catalysts and concluded that microcrystals of the nickel-copper solid solution are also formed in this case, and that the mechanism of the decrease in activity is the same as

in the first case. On this basis the author assumed that the atomic ratio of copper to nickel in the solid solution is equal to their ratio in the ternary alloy.

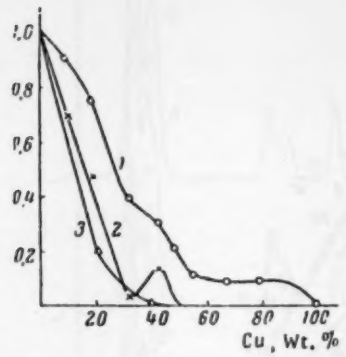

Fig. 1. Curves of dependence of the magnetic susceptibility and activity on the copper content in coprecipitated and skeletal catalysts (Cu + Ni): 1) Change of specific magnetic susceptibility in coprecipitated catalysts; 2) change of activity per g of Ni in coprecipitated catalysts in the hydrogenation of benzene in the liquid phase; 3) change of magnetic susceptibility per g of skeletal catalyst. The magnetic susceptibility and specific activity of the catalysts in the absence of copper are taken to be unity.

However, preliminary consideration of a number of properties of Al–Ni–Cu ternary alloys and the data of x-ray structural investigations, indicated that the above-mentioned conclusion of Reynolds was unwarranted. Below we give the results of a rather detailed study of this question.

Phase Diagram of Al – Ni – Cu Alloys

The phase diagram of Al–Ni–Cu alloys, which was studied by Koster et al. [9], is shown in Fig. 2.

Let us consider the phase composition of alloys for the section with 50% Al*, in which the alloys investigated by us and by Reynolds lie. From 0 to 12% copper the alloys lie in a two-phase region and consist of the ϵ-and δ-phases. The structure of the ϵ-phase is based on the compound $NiAl_3$; that of the δ-phase is based on Ni_2Al_3.

According to the phase diagram, the ϵ-phase can dissolve up to 1% copper, whereas the δ-phase can dissolve up to 35%. In the region from 12 to 20% copper a third phase appears, consisting of a solid solution based on Al. In the phase diagram given in [9] this phase is denoted as Al. To avoid confusion we shall use this notation below. In this region the amount of the ϵ-phase decreases as the Cu content increases, and is practically equal to zero at 20% copper.

Alloys with a copper content from 20 to 28% consist of δ- and Al-phases. As the copper content is further increased to 35%, there appears not nickel, but the T-phase, which consists of a solid solution based on the compound Cu_3NiAl_6; in the region from 40 to 50% copper the amount of the T-phase decreases and the Θ-phase ($CuAl_2$) appears.

From the data given, it is evident that, as the copper content in the Al–Ni–Cu alloy (50% Al) increases, the phase composition of the original alloy continually changes. The copper is very unevenly distributed among the phases: the composition of the ϵ-phase changes only slightly as the copper content increases, and practically all the copper goes into the δ-phase, the T-phase, and then the Θ-phase. It should be mentioned that the phase diagram was obtained for alloys in equilibrium. The alloys investigated by us and by Reynolds were not specially equilibrated, and hence the phase compositions and the relative amounts of each phase present are somewhat different from the equilibrium values, but the principal regularities, given above, naturally are retained.

Phase Composition of Leached-Out Al – Ni – Cu Alloys

The catalysts were prepared in the following manner: the alloys were reduced to a fine powder passing through a 200-mesh screen, leached in 20% NaOH at 98-100° until hydrogen ceased to be evolved, and washed with hot water.

The phase composition was investigated by an x-ray method. X-ray patterns of both original and leached-out alloys were taken; comparison of these x-ray patterns made it possible to gain a rather complete idea of the phase composition of the samples.

In Fig. 3 are shown diffraction patterns, obtained with a VRS-5OI ionization-type x-ray apparatus, for the region of angles in which the most intense reflections of the δ-phase and ϵ-phases, aluminum, and nickel occur.

To interpret the diffraction patterns we used the data of [10], in which x-ray patterns of various phases of the system Al–Ni are given, and [9].

*Here and below, the weight percentages are given.

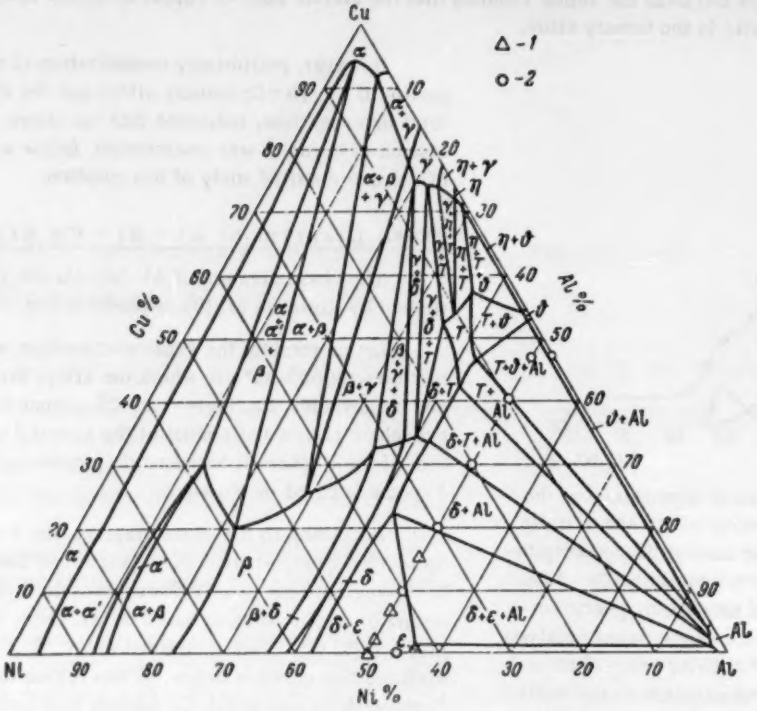

Fig. 2. Phase diagram of Al–Ni–Cu alloys according to Köster [9]. 1) Alloys investigated in the present work; 2) alloys investigated by Reynolds [3].

At 15% Cu in the δ-phase, according to the data of [9], a new δ-phase line of practically the same intensity appears to the right of the most intense line.

From the figure it is evident that in conformity with the phase diagram the amount of the ϵ-phase decreases as the copper content increases, and at 20% copper the strongest line of this phase is practically invisible. From comparison of the leached-out and original alloys a very important conclusion can be drawn: as the Cu content in the δ-phase increases, this phase becomes insoluble on leaching.

With a 10% copper content in the alloy (about 20% in the δ-phase) the δ-phase practically does not dissolve on leaching; only the ϵ- and Al-phases* dissolve. When the alloy contains 20% copper, only the Al-phase dissolves.

Catalytic Activity and Other Properties of Leached-Out Al – Ni – Cu Alloys

The method of preparation and investigation of "skeletal" catalysts is described in [1]. The specific surface was measured by the B.E.T. method through low-temperature adsorption of nitrogen. The degree of leaching-out was determined from the amount of hydrogen evolved in leaching the samples. In the table we give the results of investigation of nickel-copper "skeletal" catalysts.

The given material shows that the results obtained are qualitatively similar to Reynolds' data for similar alloys.

It is a remarkable fact, however, that the specific activity per unit surface of the catalyst changes relatively little up to a 15-20% copper content in the alloy, while the surface area falls sharply. This shows that the surface layer consists mainly of active metallic nickel. On addition of copper the degree of leaching-out of aluminum gradually falls and then rises. It is important to note that the activation energy of benzene hydrogenation on all catalyst samples remains approximately constant, contrary to Hall and Emmett's data [5] on coprecipitated nickel-copper catalysts. On samples of the latter the activation energy increased from 13 to 18.5 kcal/mole for a copper content from 15 to 60 at. %. This was one of the facts indicating the essential difference in the nature of the decrease in activity of "skeletal" and coprecipitated and nickel-copper catalysts.

*In the alloys investigated, probably owing to their nonequilibrium state (on account of rapid cooling), the Al-phase appears at copper contents lower than the phase diagram indicates.

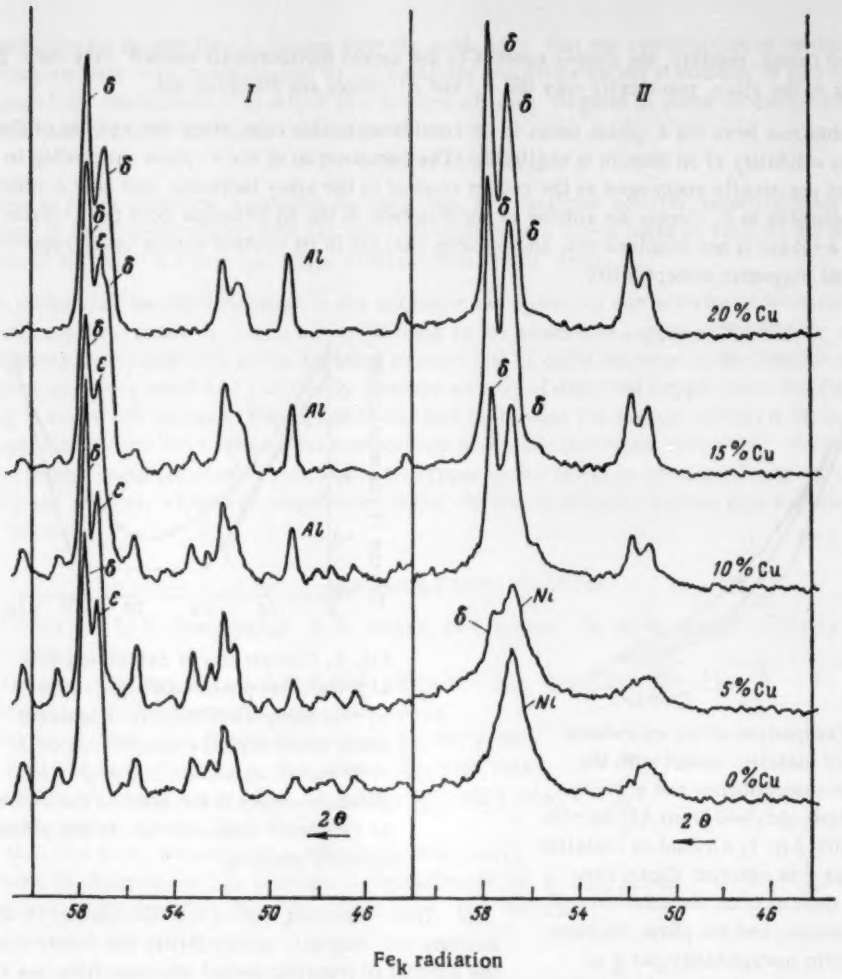

Fig. 3. Comparison of the diffraction patterns of original (I) and leached-out (II) alloys.

Copper content in the alloy, wt. %	Degree of extraction of Al, %	Specific surface of the catalyst, m^2/g	Activity at 38°*			Activation energy, kcal/mole
			% conversion of benzene	k · 10 , moles per g-hr	k · 10 , moles per m^2-hr	
0	91	80	27	1,2	1,5	11,5
3	80	90	19	0,85	0,95	12,3
5	90	67	12	0,53	0,80	11,9
10	62	23	6,7	0,2	0,87	11,2
15	42	2,5	4,5	0,02	0,80	11,0
20	45	1,8	0,12	0,005	0,28	—
25	55	29	0,05	0,0022	0,008	—
50	100	24	—	—	—	—

* $\underline{k}$ is the rate constant of benzene hydrogenation per $\underline{g}$ of catalyst (see [1]); k^1 is the specific rate constant per m^2 of surface.

DISCUSSION OF RESULTS

The magnetic susceptibility and catalytic activity of leached-out alloys depend, naturally, on both the amount of metallic nickel obtained in the form of microcrystals, and the Cu content in the solid solution.

From the aggregate of x-ray and solubility data (see table) it is evident that, up to a certain copper content in the alloy, both the alloy δ - and ε -phases are dissolved out simultaneously. The amount of copper in the δ -

phase varies, and hence, possibly, the copper content in the nickel microcrystals formed may vary. But even with 10% copper in the alloy, practically only the ϵ - and Al-phases are dissolved out.

Only Ni obtained from the ϵ -phase needs to be considered in this case, since the amount of the Al-phase is small, and the solubility of Ni therein is negligible. The composition of the ϵ -phase, according to literature data [9], remains practically unchanged as the copper content in the alloy increases, and only a little copper (about 1%) can dissolve in it. Hence the amount of Cu dissolved in the Ni obtained from the ϵ -phase will be small when the δ -phase is not dissolved out, and possible changes in its content cannot cause appreciable changes in its activity and magnetic susceptibility.

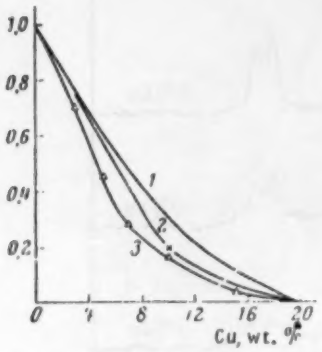

Fig. 4. Comparison of the calculated amount of metallic nickel with the magnetic susceptibility and activity for catalysts obtained from Al–Ni–Cu alloys (50% Al): 1) Amount of metallic nickel per g of catalyst. Curve constructed from data on the solubility of various phases, and the phase diagram; 2) magnetic susceptibility per g of catalyst according to Reynolds' data [3]; 3) catalytic activity per g of catalyst.

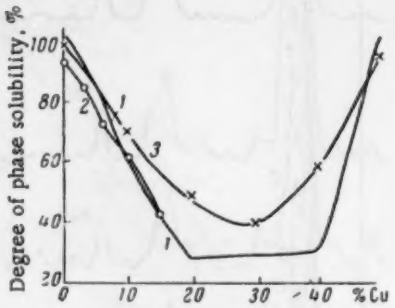

Fig. 5. Comparison of calculated and experimental phase solubilities of Al–Ni–Cu alloys (50% Al): 1) Calculated phase solubility; 2) experimental data; 3) Reynolds' data [3]. (The degree of phase solubility is the ratio of the amount of aluminum dissolved out to the amount initially present).

Thus, beginning with a 10% Cu content in the alloy, the activity and magnetic susceptibility are determined only by the amount of metallic nickel obtained from the ϵ -phase, i.e., in the final analysis – the amount of the ϵ -phase.

With a 20% copper content in the alloy, according to the phase diagram and our x-ray patterns, the ϵ -phase has practically vanished. Hence with this copper content both the activity and magnetic susceptibility should be practically zero.

Changes of catalytic activity and magnetic susceptibility present the same picture (Fig. 4).

Using the phase diagram and the data on the solubility of various phases described above, we constructed an approximate graph (from three points–0, 10, and 20% Cu) of the relation between the amount of metallic nickel per g of leached-out alloy and the copper content, and compared it with data obtained on the catalytic activity, and magnetic susceptibility data [3]. Results of the comparison are given in Fig. 4. It is evident that both the magnetic susceptibility and catalytic activity are practically proportional to the amount of nickel obtained from the dissolved-out phases. This result is quite natural and confirms the correctness of the reasoning given above; moreover, it follows from this that the ratio of the amount of the δ -phase to that of the ϵ -phase is nearly the same for annealed as for quickly cooled alloys.

Calculated and experimental solubility curves are compared in Fig. 5. The calculated curve is constructed from the points for 0, 10, 20, 40, and 50% copper, proceeding from data on the solubility of various phases and their relative amounts determined from the phase diagram. It is assumed that the T-phase is insoluble. It is evident not only that the curves coincide qualitatively, but also that the quantitative data are quite close; this shows that the change in solubility also is fully explained by the change in phase composition.

In conclusion let us note how it follows from the work done that the combination of structural investigations and phase-diagram data with investigations of the catalytic properties makes it possible to resolve certain complex questions of the mechanism of catalysis in a number of cases. Neglect of phase investigations leads, as is evident in the case of [3], to erroneous conclusions.

SUMMARY

Changes in phase solubility, magnetic susceptibility, and catalytic activity, resulting from change in the copper content in Al–Cu–Ni alloys (50% Al), are explained from a single point of view on the basis of x-ray investigations of Al–Ni–Cu alloys and phase-diagram data on the latter.

It was shown that the rapid decrease in the magnetic susceptibility and activity of leached-out alloys with increase in the copper content is caused not by increase in the amount of copper in the Ni–Cu solid solution formed, according to Reynolds [3], in the leaching process, but by rapid decrease in the amount of metallic nickel, which can contain a very small and practically constant amount of dissolved copper when the Cu content in the ternary alloy is about 10% or more. This is due to the fact that, when the copper content is about 10%, metallic nickel is formed only from the ϵ-phase; the composition of the latter remains unchanged, whereas the amount of it rapidly decreases, being practically zero with 20% copper in the alloy. In correspondence with this, the magnetic susceptibility and activity, which are proportional to the amount of metallic nickel, also approximate zero with this copper content.

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DEHYDROGENATION OF ISOPENTANE BY CHROMIUM OXIDE-ALUMINUM OXIDE CATALYSTS

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The dehydrogenation of isopentane in a boiling bed by a chromium-aluminum catalyst was investigated, with analysis of the products by chromatographic methods. The behavior of catalysts of different composition in a stationary and a boiling bed was investigated: the activity of the catalysts investigated depended little on their composition; the yield of isoamylene and isoprene at 550° was 30-31% on the isopentane. The kinetic laws of the process for the region of small conversions of isopentane were established; the surface of the catalyst was occupied by amylenes and isoprene, the observed activation energy was 44 kcal/mole. In a boiling bed at 600° and 100 mm Hg the isoprene yield was 15% on the isopentane, the isoprene content in the C_5 fraction was 21%.

The dehydrogenation of isopentane by oxide catalysts was examined in [1-5]. Information on the process was usually obtained by determining the total unsaturation of the products. Since the latter contain very different hydrocarbons, this characteristic is insufficient for assessing the process.

The present communication gives the results of investigations on the dehydrogenation of isopentane by chromium oxide-aluminum oxide catalysts, with chromatographic analysis of the products. For a comparative assessment of different catalysts a series of experiments was carried out with a stationary catalyst with a particle size of 0.25-0.5 mm.

The kinetics of the process were investigated in a vacuum apparatus with a boiling bed of size 0.05-0.1 mm catalyst, where, by reason of resultant mixing, isothermal conditions are maintained and all the particles are under the same conditions of suspension by gas.

Equilibrium of Dehydrogenation Reactions of Isopentane

The equilibrium constants of dehydrogenation reactions of isopentane to isoamylenes and isoprene, calculated according to the data of [6] for temperatures of 427-627°, are given in Table 1. The equilibrium composition of the products at a pressure of 760 and 100 mm Hg are given in Fig. 1 and 2. In the 500-600° range an increase in temperature leads to a considerable increase in the equilibrium yield of isoamylenes. A reduction in pressure increases the isoprene yield; at 602° and 100 mm Hg it is thermodynamically possible to decompose almost completely the isopentane, with 51.7% and 46.5% yields of isopentane and isoprene respectively.

EXPERIMENTAL

When the experiments were carried out in a stationary bed, 20 ml of catalyst was placed in a quartz tube with a thermocouple pocket, heated by an electric oven. Before the experiment the catalyst was activated with hydrogen for an hour. Isopentane was fed from a thermostatically controlled cylinder, the products were condensed

TABLE 1

Equilibrium Constants of Dehydrogenation Reactions of Isopentane

Reaction	$K_{427°}$	$K_{477°}$	$K_{527°}$	$K_{577°}$	$K_{627°}$
iso-$C_5H_{12} \rightleftarrows CH_2=C(CH_3)-CH_2-CH_3 + H_2$	0,0147	0,0588	0,209	0,610	1,668
iso-$C_5H_{12} \rightleftarrows CH_2=CH-CH(CH_3)-CH_3 + H_2$	0,00185	0,00842	0,0323	0,1044	0,303
iso-$C_5H_{12} \rightleftarrows CH_3-C(CH_3)=CH-CH_3 + H_2$	0,0221	0,0816	0,255	0,698	1,739
$CH_3-C(CH_3)-CH-CH_3 \rightleftarrows$ $\rightleftarrows CH_2=C(CH_3)-CH=CH_2 + H_2$	0,00158	0,00974	0,0254	0,1043	0,220

over dry ice and acetone, and the uncondensed gases were collected in a suitable vessel. Samples of the liquid products were taken in ampoules and subjected to chromatographic separation, the gases were analyzed in a VTI apparatus and their density was determined. The catalyst coke was burnt in a current of air and the amount of carbon was determined from the composition of the gas obtained.

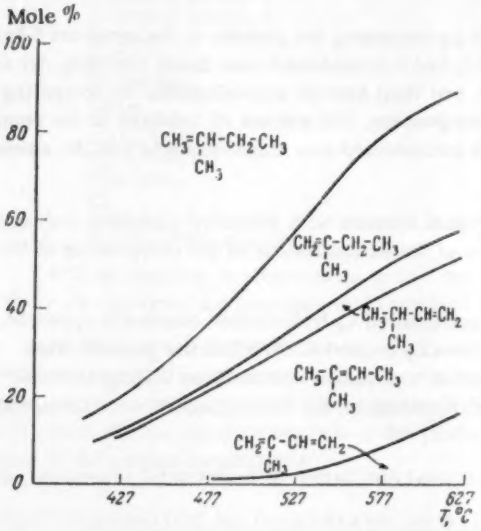

Fig. 1. Equilibrium composition of the dehydrogenation products of isopentane at atmospheric pressure.

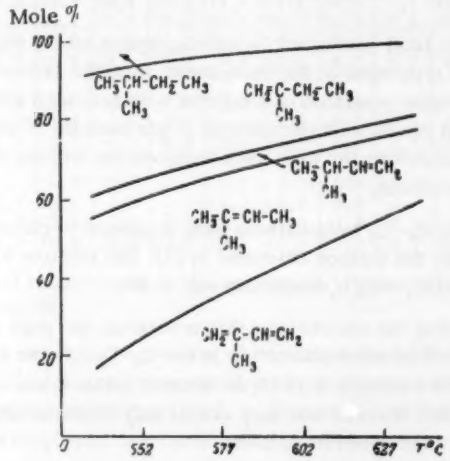

Fig. 2. Equilibrium composition of the dehydrogenation products of isopentane at a residual pressure of 100 mm Hg.

A diagram of the vacuum apparatus with a boiling bed of catalyst is shown in Fig. 3. The reactor 1—a quartz tube with an electric winding—had a diameter of 21 mm with a widened upper part and a thermocouple pocket. Quartz fragments and 10-20 ml of catalyst were distributed over a chamotte grid fixed in the pocket; the catalyst was dried, and it was then activated in the same way as for the apparatus with a stationary bed. Isopentane was fed from a thermostatically controlled cylinder 2 at a temperature of 40°, which ensured constant consumption. The reaction products were fed into pre-evacuated flasks 4, via a special valve [7] for maintaining the pressure in the reactor 3, which had proved very satisfactory under similar conditions [8]; the products were then analyzed by a system forming an integral part of the apparatus.

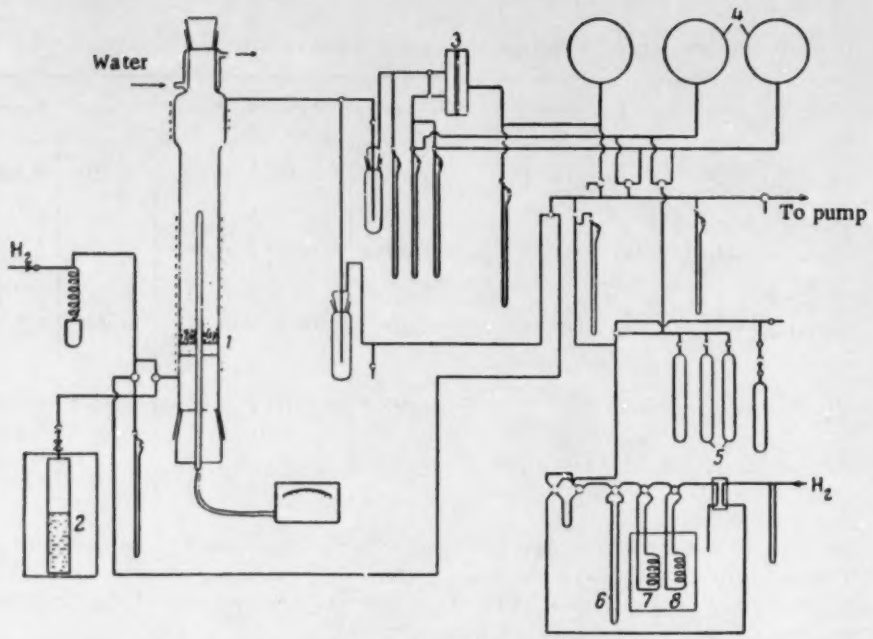

Fig. 3. Diagram of the vacuum apparatus for dehydrogenation of isopentane in a boiling bed.

The total content of C_2 and C_{2+} hydrocarbons was found by measuring the pressure in the receivers 5 before and after separation of the components from the products which had not condensed over liquid nitrogen. Air and methane were separated in a column with activated charcoal, and their amount was calculated by comparing the analytical results with the analysis of gas samples of known composition. The amount of hydrogen in the products was calculated by the difference between the amount of gases uncondensed over liquid nitrogen and the amount of air + methane.

The C_2 - C_5 hydrocarbons were separated in chromatographic columns with diisoamyl phthalate and acetonyl acetone by the method described in [9]. The relative accuracy of the determination of the composition of the mixture of C_1 - C_5 hydrocarbons was 3-4%.

During the chromatographic separation the peak of an unidentified C_6 hydrocarbon constantly appeared. The content of this hydrocarbon in the C_2-C_5 mixture did not usually exceed 0.5%. When the products were distilled in a column with 30 theoretical plates it was not possible to separate hydrocarbons boiling above 40° because their amount was very small; only hydrocarbons which appeared on the chromatogram were taken into account in the material balance.

The initial isopentane, obtained by purification and fractional distillation of commercial isopentane, did not contain chromatographically determinable impurities.

Catalysts of different composition were used for the comparative assessment. Sample 1 contained 14.8 wt. % Cr_2O_3, 83.7 wt. % Al_2O_3 and 1.5 wt. % K_2O. Sample 2 contained 7.0 wt. % Cr_2O_3, 92.5 wt. % Al_2O_3 and 0.5 wt. % K_2O. Sample 3 was synthesized in B. A. Kazanskii's laboratory and its properties are described in [3].

The experiments for the comparative assessment of different catalysts were carried out with the same sample of catalyst, which was regenerated after each cycle in a current of air at 480°. Measurements on this sample were carried out after several dehydrogenation and regeneration cycles, as a result of which the activity reached a stable value.

To avoid errors due to the slight variation in the stability, the experiments in a boiling bed and the comparative kinetic experiments in a stationary bed were carried out on fresh samples of catalyst. Sample 2 was used in these experiments.

Dehydrogenation of Isopentane in a Stationary Bed

Table 2 gives the composition of the products of the dehydrogenation of isopentane by different catalysts in a stationary bed. The data of the Table show that the activities of all the samples are similar in value. At 550° and a volumetric rate of the order of 1, practically similar results were obtained in all cases, the yield of isoamylenes calculated on the isopentane feed was 27.6-29%, the isoprene yield was 1.5-2.5%, the degree of isopentane conversion was 46-47%; the selectivity, calculated as the ratio between the yield of isoamylenes and isoprene and the amount of unreacted isopentane, was 65-67%. Calculated on 100 moles of reacted isopentane, about 10 moles was consumed on the formation of normal C_5 hydrocarbons and about 20 moles on the formation of C_1 - C_4 hydrocarbons.

TABLE 2

Dehydrogenation of Isopentane in a Stationary Bed by Catalysts of Different Composition

Experimental conditions and composition of the products	t = 520°		t = 550°			t = 580°				
	sample		sample			sample				
	1	2	1	2	3	1		2	3	
Volumetric rate	1,01	1,15	1,12	0,96	0,95	0,61	2,74	2,30	0,44	1,67
Degree of conversion, mole %	28,1	27,6	47,0	45,5	46,5	74,4	60,7	54,3	73,4	48,2
Selectivity, %	79,3	81 9	65,6	66,2	65,9	39,5	61,7	69,0	45,1	64,2
Yield of isoamylenes, mole %	21,2	21,2	28,5	27,6	29,2	26,7	33,0	32,8	31,5	27,4
Isoprene yield, mole %	1,1	1,3	2,3	2 5	1,4	2,7	4,5	4,6	1,6	3,6
Distribution of reacted isopentane in the reaction products, %										
Isoamylenes	75,5	77,2	60,7	60,6	62,9	35,9	54,3	60.5	42,9	56,8
Including:										
3-methyl butene-1	11,1	10,5	6,2	5,6	5,2	5,7	6,9	9,2	5,8	6,5
2-methyl butene-1	20,3	24,2	18,1	20,4	19,2	11,1	17,1	18,1	12,3	16,9
2-methyl butene-2	44,1	42,5	36,4	34,6	38,5	19,1	30,3	33,2	28,4	33,4
Isoprene	3,8	4,7	4,9	5,6	3,0	3,6	7,4	8,5	2,2	7,4
n-C_5,	8,9	4,7	9,9	10,5	6,3	9,1	11,0	8,1	6,3	4,8
Including:										
C_5H_{12}	2,5	1,0	2,9	2,7	2,4	2,3	2,1	1,2	2,1	0,5
C_5H_{10}-1	0,9	0,8	1,4	1,6	1,1	1,3	1,7	1,0	0,7	0,5
C_5H_{10}-2 (Trans.)	3,0	1,9	3,1	3,5	2,2	3,2	4,2	3,3	2,1	2,8
C_5H_{10}-2 (Cis)	2,5	1,0	1,7	2,0	0,6	1,9	2,0	2,0	1,1	1,8
Piperylene	—	—	0,8	0,7	—	0,4	1,0	0,6	—	—2
C_6	0,6	0,7	1,1	1,1	—	1,3	2,7	1,5	—	—0
Coke	2,6	1,2	3,5	2,3	5,8	16,4	4,8	4,4	15,9	8,5
C_1–C_4 hydrocarbons	8,9	11,5	19,9	19,9	22,0	33,7	19,8	17,0	32,7	22,5

With an increase in temperature to 580° the yield of isoamylenes on the isopentane introduced rose to 31-33% for all catalysts, the isoprene yield increased to 3.5-4.6%.

At 520° and a volumetric rate of ~1, for samples 1 and 2 the conversion of isopentane was 28%, the yield of isoamylenes and isoprene was 23%. Thus, the total yield of isoamylenes and isoprene in these conditions was far less than the values given in the literature [1-5], but in a recent report by B. A. Kazanskii and his co-workers [10], where chromatographic analysis of the products was employed, the results obtained were similar to those found in the present investigation.

Dehydrogenation of Isopentane in a Stationary and a Boiling Bed in the Region of Low Conversions

To investigate the kinetics of the process and the composition of the products at low conversions of isopentane, a series of experiments was carried out at 500, 520 and 550° and pressures of 100, 300 and 500 mm Hg in a boiling bed and 760 mm Hg in a stationary bed.

Fig. 4 and 5 give typical curves of the distribution of the reaction products. The degree of conversion χ is plotted on the abscissa; the difference of the ordinates between two neighboring curves, y/y, is equal to the number of moles of isopentane consumed on the formation of the product.

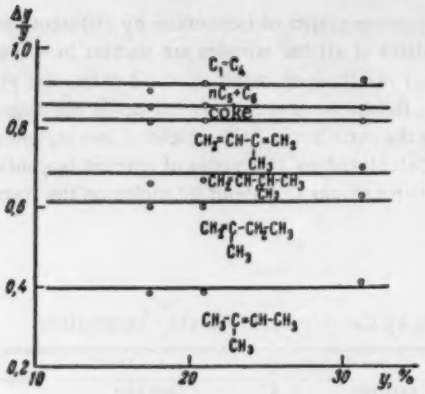

Fig. 4. Distribution of the reaction products of the dehydrogenation of isopentane at 550° and a pressure of 300 mm Hg in a boiling bed.

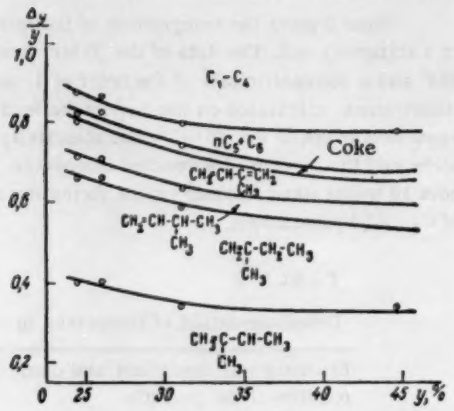

Fig. 5. Distribution of the reaction products of the dehydrogenation of isopentane at 550° and a pressure of 760 mm Hg in a stationary bed.

At the same temperature the ratio between the isoamylenes remained constant, irrespective of the contact time and the degree of conversion of isopentane, i.e. 2-methyl butene-2, 2-methyl butene-1 and 3-methyl butene-1 and 3-methyl butene-1 were present in the mixture of products in the ratio of 100: 50: 16.5 at 500° and 100: 55: 16 at 550°.

When special experiments were carried out in which isoamylenes of different initial composition were passed over the catalyst at 580° (Table 3), the ratio between the isoamylenes was practically independent of the composition of the initial mixture. It follows, therefore, that isomerization reactions of isoamylenes by oxide catalysts take place at high velocity.

TABLE 3

Experiments with Isoamylenes at 580° and 300 mm Hg

Content of isoamylenes, %	Initial fraction	Reaction products, t = 0.44 sec.	Initial fraction	Reaction products, t = 0.54 sec.	Reaction products, t = 0.57 sec.
A) 2-methyl butene-2	94.7	25.2	3.8	26.9	25.2
B) 2-methyl butene-1	2.1	14.2	65.9	16.3	14.8
C) 3-methyl butene-1	—	3.4	28.5	3.6	3.6
Ratio A: B: C		100: 56: 13		100: 61: 13	100: 59: 14

Within the limits of experimental error the ratio between the total isoamylenes, isoprene and hydrogen agreed with the equilibrium value. The dehydrogenation of isoamylenes by chromium-aluminum catalysts therefore takes place very rapidly.

At low conversions, the C_1: C_4: and C_2: C_3 molar ratios in the dehydrogenation products differ little from unity: it may therefore be assumed that the C_1 -C_4 hydrocarbons were formed mainly during the cracking of isopentane. On this assumption, as is shown by calculation, at 500°, 520° and 550°, 2-4%, 3-10% and 6-12% respectively of the total amount of reacted isopentane is consumed in the cracking reaction. At the same time, the selectivity at 500°, 520° and 550° is 83-90%, 80-86% and 76-83% respectively, i.e. the reduction in the selectivity coincides approximately with the increase in the consumption of isopentane in the cracking reaction.

Kinetic Features of the Dehydrogenation Reaction of Isopentane

The composition of the dehydrogenation products of isopentane varies together with the extent of conversion, i.e. the stoichiometric coefficients ν of the equation

$$\text{iso-}C_6H_{12} \rightarrow \sum_{i=1}^{m} \nu_i A_i \quad i = 1, 2, 3, \ldots, m, \tag{1}$$

where A_i are the reaction products, depend on temperature, pressure and contact time. To integrate the differential equations of the kinetics of the process it is necessary to know the form of these relations. In principle, the investigation of a process in a boiling bed under conditions of complete mixing of the gas [11-12], where the concentrations are the same throughout the bed and agree with the concentrations at the outlet from the bed, is far simpler. In this case the partial pressure of isopentane p_0 can be determined from the equation

$$\omega_0 P - \omega p_0 = lh, \tag{2}$$

where ω_0 is the linear velocity of isopentane under the experimental conditions before entering the bed; ω is the rate of movement of the gas in the bed, calculated on the cross section free from catalyst; P is the pressure in the system; l is the height of the bed; $\underline{h}$ is the amount of reacted isopentane per unit volume of bed in unit time.

When the experimental data were examined the following equation was used for the velocity of the process [13-14]:

$$h = k' S \frac{a_0 p_0}{1 + a_0 p_0 + \sum_1^m a_i p_i}, \tag{3}$$

where S is the catalyst surface per unit volume; a_0 is the adsorption coefficient of isopentane; a_i and p_i are the adsorption coefficients and the partial pressures of the products; k' is a constant.

Equation (3) was derived for irreversible reactions. As was shown by calculations, under the experimental conditions in all cases the velocity of a reversible reaction was not more than 4-6% of the velocity of a direct reaction. Joint solution of equations (2) and (3), with account taken of the relationships

$$y = \frac{\omega_0 P - \omega p_0}{\omega_0 P}; \qquad p_0 = \frac{P(1-y)}{1 + (\nu - 1) y}; \qquad p_i = \frac{P \nu_i y}{1 + (\nu - 1) y};$$
$$S = k''(1 - \varepsilon).$$

[where ν_i is the stoichiometric coefficient in the right-hand part of equation (1); $\nu = \sum_1^m \nu_i$ is the number of moles of products per mole of isopentane; ϵ is the porosity of the bed] leads to the following equation:

$$\left(1 - \beta + \frac{y}{1-y}\right) y = \frac{k''' a_0 t}{\nu + P \sum_1^m \nu_i a_i}. \tag{4}$$

Here $k''' = k'k''$; $t = \frac{l(1-\epsilon)}{\omega_0}$ is the contact time,

$$\beta = 1 - \frac{1 + a_0 p_0}{\nu + P \sum_1^m \nu_i a_i}. \tag{5}$$

If the reaction products are intensely adsorbed on the surface ($a_i \rightarrow \infty$), $\beta \cong 1$ and equation (4) can be written in the form

$$\left(\sum_1^m \nu_i a_i\right)\frac{y^2}{1-y} = \frac{k''' a_0 t}{P} \qquad (6)$$

At constant value of the sum $\sum_1^m \nu_i a_i$, the relation between $y^2/(1-y)$ and t/p must be linear. A preliminary study showed that the experimental points on graphs of this type lie near the straight lines, independently of the pressure and degree of conversion, i.e. the reaction is retarded by the product formed.

The principal reaction products of the dehydrogenation of isopentane at low conversions are isoamylenes, isoprene and hydrogen. In [15, 16] it was shown that the dehydrogenation reaction of butane is slightly retarded by hydrogen. For this reason, in the sum $\sum_1^m \nu_i a_i$ the two terms $\nu_1 a_1 + \nu_2 a_2$, where the index 1 refers to isoamylenes, and 2 to isoprene, may be retained. Under the experimental conditions the ν_1/ν_2 ratio was measured 2-2.5 times, but the isoprene content was 4-10-fold less than the content of isoamylenes. With this isoprene content, the constant of equation (6) varies by 10% only when $a_2/a_1 = 2$ or $a_2/a_1 = 0.2$. Deviations were not found in the values of the constant for different pressures. It follows, therefore, that the a_2/a_1 ratio did not exceed 2. When the experimental results were studied the adsorption coefficients of isoamylenes and isoprene were assumed to be the same. This assumption may lead to a variation of the constant by 5%. At $a_1 = a_2$ (6) assumes the form

$$\frac{xy^2}{1-y} = \frac{kt}{P}, \qquad (7)$$

for $x = \nu_1 + \nu_2$; $k\frac{k''' a_0}{a_1}$ – is a constant, independent of temperature.

The experimental data for a boiling bed, used in evaluating equation (7), are given in Fig. 6. As may be seen from the graph, the experimental points lie on straight lines within the corresponding coordinates, irrespective of the pressure and the contact time.

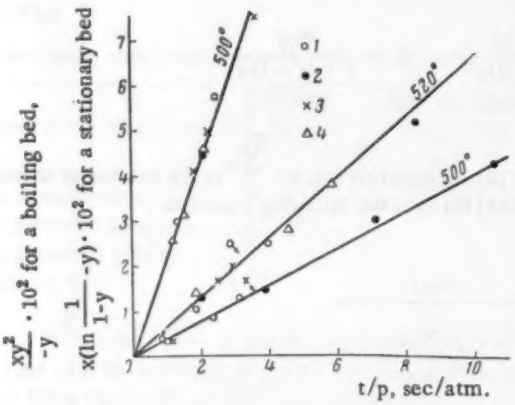

Fig. 6. Kinetic curves of the dehydrogenation of isopentane in a stationary and a boiling bed in the region of low conversions: 1) 100 mm Hg, boiling bed; 2) 300 mm Hg, boiling bed; 3) 50° mm Hg, boiling bed; 4) atmospheric pressure, stationary bed.

Fig. 6. also shows the points plotted from experimental data for a stationary bed at low conversions of isopentane. The differential equation of the kinetics of the process in a stationary bed

$$-\frac{d(\omega p_0)}{dl} = h, \qquad P = p_0, \quad \text{for } l = 0 \qquad (8)$$

is directly integrated in the case where the stoichiometric coefficients of equation (1) do not vary with the extent of conversion. From Fig. 4 and 5 it is seen that in the region of low conversions the composition of the reaction products depends little on the degree of conversion. The solution of equation (8) for h, as determined by (3), is given in [13, 14]. In the symbols used in the present article it has the form:

$$\ln\frac{1}{1-y} - \beta y = \frac{k''' a_0 t}{\nu + P\sum_1^m a_i \nu_i} \qquad (9)$$

The left-hand part of equation (9) with an accuracy taking amount of terms up to the order of y^3 is equal to $(1-\beta)\,y + y^2/2$. With the same degree of accuracy the left-hand part of equation (4) is equal to $(1-\beta)\,y + y^2$. Thus, if we limit ourselves to terms of the first order the kinetic curves for conditions with or without mixing are the same. The kinetic curves also have the same appearance in the $y^3 \ll y^2$ region and likewise $y^2 \gg (1-\beta)y$, but

in this case the numerical value of the constant for conditions in which mixing is absent, found by means of equation (9), is twice as great as for conditions with complete mixing.

When the results of experiments in a stationary and boiling bed were compared it was found that the numerical values of the constants, found respectively from equations (7) or (9) with $\beta = 1$, differ by approximately 100%. It followed, therefore, that conditions similar to complete mixing are present in a boiling bed; for this reason, when the data for a boiling bed were examined equation (7) was used. The analysis of the data for a stationary bed was carried out with respect to equation (9), which at $\beta = 1$ and $a_1 = a_2$ assumes the form

$$x\left(\ln\frac{1}{1-y} - y\right) = \frac{kt}{p}. \qquad (10)$$

The experimental points for a stationary and a boiling bed, described by completely different equations, are grouped around the same straight lines passing through the origin of the coordinates (Fig. 6), the position of which is determined by the tangent of the angle of slope, equal to the constant k.

The comparison of experimental results for a stationary and a boiling bed allows the conclusion to be drawn that with a catalyst of particle size 0.5 mm and at a temperature of 550° the process lies in the inner kinetic region, because it is described by the same laws with the same constant for both coarse and fine particles.

The value of the constant k was calculated from the tangent of the angle of slope of the straight lines in Fig. 6. It was $3.87 \cdot 10^{-3}$ atm/sec at 500°, $6.72 \cdot 10^{-3}$ atm/sec at 520° and $21.8 \cdot 10^{-3}$ atm/sec at 550°. The mean deviation of the experimental points from the straight lines (7, 10) in Fig. 6 at the indicated values of k was 5%. The observed activation energy, found from the graph of the relation between log k and the reciprocal of the temperature, was 44 kcal/mole.

The process is described by equations (7) and (10), obtained from the conditions $(1-\beta) \gg y$, at least when $y = 0.1$. Having assessed $(1-\beta) = 0.1\ y$ and assumed that $y = 0.1$, it can be concluded from (5) that the adsorption coefficient of isoamylenes is 2 orders higher than that of isopentane.

Dehydrogenation of Isopentane at Elevated Temperatures and Reduced Pressures

Table 4 gives the results of experiments on the dehydrogenation of isopentane in a boiling bed to determine the possibilities of single-stage production of isoprene from isopentane.

Equalization of the concentrations in a boiling bed leads to retardation of the process and an increase in the proportion of secondary and side reactions [12]. It may be noted that the same effects must also occur during work with a granulated catalyst [17], because the reduction in selectivity as a result of diffusion retardation and retardation by mixing is due to the non-uniformity of the residence of the molecules in the reaction zone. Although the experimental conditions are not optimum from this aspect, the isoprene yield per "run" is fairly high, as may be seen from Table 4. At 600°, 100 mm Hg and a contact time of 2.2 sec, 20.2% of the decomposed isopentane was converted to isoamylenes, and 15.3% to isoprene; the isoprene content in the C_5 fraction was 21%.

The most favorable conditions for single-stage dehydrogenation of isopentane to isoprene are evidently those of a boiling bed without reverse mixing of the reagents. In a boiling bed it is comparatively easy to supply the large amounts of heat necessary for the intensely endometric dehydrogenation reaction. By selecting appropriate hydrodynamic conditions [12], for example by increasing the gas velocity and the height of the reactor, conditions can be established in which the degree of reverse mixing is only slight. By carrying out a process in a boiling bed without retardation by mixing and without diffusion retardation it is possible to obtain a maximum isoprene yield.

The authors wish to express their thanks to B. A. Kazanskii for discussing the results of this investigation.

SUMMARY

1. The dehydrogenation reaction of isopentane in a stationary and a boiling bed was investigated, with analysis of the products by chromatographic methods.

2. A comparative assessment was made of catalysts of different composition in a stationary bed. The ca-

TABLE 4

Dehydrogenation of Isopentane in a Boiling Bed

Experimental conditions and composition of the products	Pressure, mm Hg					Pressure, mm Hg					
	100			300		100			300		
Contact time, sec	2,20	0,98	0,39	1,83	1,36	1,57	0,79	0,44	1,30	0,83	0,30
	At 600°					At 580°					
Degree of conversion, mole%	62,2	50,4	40,1	54,9	49,3	50,3	39,1	32,5	41,2	35,8	22,5
Selectivity, %	57,0	59,4	65,3	59,6	59,8	63,2	65,9	73,7	63,9	76,2	76,6
Yield of isoamylenes, mole %	20,2	17,7	15,3	25,0	22,2	21,0	16,0	15,5	20,9	21,1	13,3
Isoprene yield, mole %	15,3	12,2	10,9	7,6	7,3	10,8	9,8	8,5	5,1	6,1	4,0
Distribution of the reaction, mole %											
Isoamylenes	32,4	35,1	38,2	45,7	45,0	41,7	40,9	47,6	50,8	59,1	58,9
Including:											
3-methyl butene-1	2,4	2,8	4,5	6,9	6,4	3,7	4,4	4,9	6,2	4,3	3,6
2-methyl butene-1	10,8	11,6	11,9	14,6	14,0	13,3	13,3	15,8	16,9	20,6	21,7
2-methyl butene-2	19,2	20,7	21,8	24,2	24,6	24,7	23,2	26,9	27,7	34,2	33,6
Isoprene	24,6	24,3	27,1	13,9	14,8	21,5	25,0	26,1	12,3	17,1	17,7
n -C_5	1,9	2,0	2,0	6,2	3,1	4,2	1,9	1,9	4,5	5,5	2,6
Including:											
n -C_5H_{12}	0,2	0,2	0,2	0,6	0,3	—	0,2	0,3	0,5	0,4	0,2
C_5H_{10}-1	0,4	0,5	0,4	0,9	0,6	0,9	0,4	0,5	0,6	0,7	0,3
C_5H_{10}-2 (Trans.)	0,7	0,8	0,9	2,2	1,2	1,4	0,8	0,6	1,8	2,1	0,8
C_5H_{10}-2 (Cis)	0,6	0,5	0,5	1,3	1,0	0,9	0,5	0,5	1,2	1,0	0,6
Piperylene	—	—	—	1,2	—	1,0	—	—	0,4	1,3	0,7
C_6	3,5	5,7	2,0	2,4	2,0	3,6	3,1	2,6	2,6	3,4	1,6
Coke	11,4	12,2	9,4	6,4	7,0	13,6	8,9	8,8	7,0	7,2	3,0
Hydrocarbons C_1–C_4	26,2	20,7	21,3	25,4	28,1	15,4	20,2	13,0	22,8	7,7	16,2
Including											
C_1	2,1	2,8	1,6	2,5	3,1	2,2	2,5	1,5	2,1	1,0	2,4
C_2	6,7	4,3	4,5	6,1	6,5	3,3	4,5	2,9	5,0	1,7	2,8
C_3	10,0	8,3	8,5	8,7	9,8	5,2	7,6	5,1	8,0	2,6	3,6
C_4	7,4	5,3	6,7	8,1	8,7	4,7	5,6	3,5	7,7	2,4	7,4

talysts had similar activities. Isoamylenes and isoprene were obtained in 30-31% yield with 46-47% conversion of isopentane and a temperature of 550°, and with a yield of 22-23% in the case of 28% isopentane conversion and a temperature of 520°.

3. The kinetics of the dehydrogenation of isopentane in the region of low conversions (up to 30%) were investigated. The process is described by a kinetic equation derived from the condition of uniformity of the catalyst surface. The latter is occupied by the product. The observed activation energy is 44 kcal/mole.

4. At 600° and a pressure of 100 mm Hg in the reactor, with complete mixing, the isoprene yield, calculated on the isopentane feed, was 15% and the isoprene content in the C_5 fraction was 21%. It is suggested that the conditions of a boiling bed without reverse mixing of the reagents are the most favorable for single-stage preparation of isoprene.

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ON THE SELECTIVITY OF ACTION OF ZINC CATALYST IN HYDROGENATION REACTIONS OF MONO- AND DIOLEFIN HYDROCARBONS

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It has been established that zinc selectively catalyzes the hydrogenation of the ethylenic bond in styrene at normal pressure and the conjugated double bond at elevated pressures. The aromatic bond and the nonactivated ethylenic bond are not hydrogenated on zinc.

As was shown earlier [1, 2], metallic zinc in skeletal form selectively catalyzes the hydrogenation of the triple bond to a double bond: acetylene to ethylene, tolan to stilbene, vinylacetylene to divinyl, and isopropenylacetylene to isoprene. Therefore zinc cannot catalyze the hydrogenation of the mono- and diolefinic hydrocarbons formed in these reactions, at normal pressure.

The activity of zinc catalyst in the hydrogenation of double bonds of variable reactivity: in cyclohexene, octene, styrene, isoprene, and piperylene, was studied in the present work.

The method of preparing skeletal zinc catalyst was described in [3]. We estimated the degree of hydrogenation of the hydrocarbon from the change of unsaturation of the product, determined by the hydrogenation or bromination method.

Octene-1 and cyclohexene did not add on hydrogen at 100 atm and 150°.

Freshly distilled styrene (b.p. 42° at 10 mm, n_D^{20} 1.5459, d_4^{20} 0.9090) was hydrogenated in a current at atmospheric pressure. In the experiment 20 ml of styrene was passed at a rate of 0.3 ml/min. The catalyst volume was 50 ml.

The temperature dependence of the yield of ethylbenzene is shown in Fig. 1. From Fig. 1 it is evident that styrene begins to add on hydrogen only at temperatures above 100°. Up to 170° the degree of conversion is small. Above 170° the rate of styrene hydrogenation sharply increases. At 220° a nearly quantitative yield of ethylbenzene (98%) was obtained. The product had: b.p. 136°, n_D^{20} 1.4955, d_4^{20} 0.8620.

Isoprene and piperylene were isolated from the technical products by distillation in a column with 70 t.p. The isoprene had: b.p. 34° at 750 mm, n_D^{20} 1.4208; d_4^{20} 0.6770, whereas the piperylene had: b.p. 41.8° at 745 mm, n_D^{20} 1.4336 and d_4^{20} 0.6802.

It was found that isoprene and piperylene do not add on hydrogen at atmospheric pressure on zinc catalyst in the temperature interval 60-140°. Therefore subsequent experiments were performed under pressure in a rotary autoclave. The catalyst volume was 60-70 ml. Hydrogen absorption continued for 3-4 hours. After removal of the catalyst the catalyzate was dried over anhydrous potash and distilled. The product obtained from isoprene hydrogenation distilled almost entirely in the interval 20-38.6°. The unsaturation of the distilled catalyzate was then determined and the degree of hydrogenation of the diene calculated.

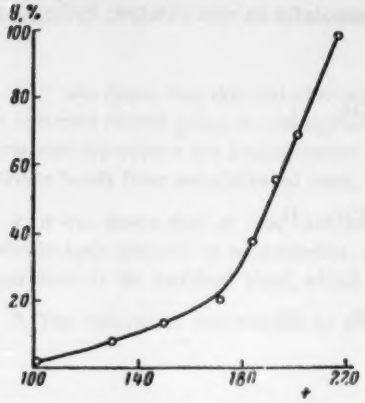


Fig. 1. Relation between the degree of hydrogenation (y) of styrene to ethylbenzene and the temperature.

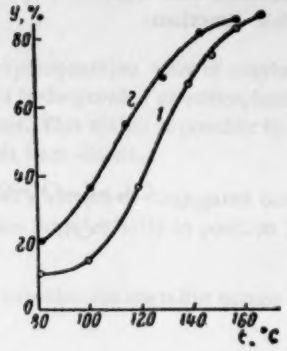


Fig. 2. Relation between the degree of hydrogenation (y) of isoprene (1) and piperylene (2) to pentenes and the temperature.

From Fig. 2 (Curve 1) it is evident that hydrogenation of isoprene under pressure begins below 80°. The reaction goes rapidly in the interval 100-140°. At 160° the unsaturation of the catalyzate fell to 57% of the original value, calculated for the diene. For identification of the hydrocarbons formed, an experiment was carried out in which 30.4 g of isoprene was hydrogenated at 160° and 100 atm initial hydrogen pressure. The catalyst volume was 60 ml. The reaction time was 3.5 hours. The final pressure was 68 atm. The unreacted isoprene was separated from the catalyst, in the form of the maleic anhydride adduct. The remaining hydrocarbon mixture was precisely fractionated in a column with an efficiency of 70 t.p.

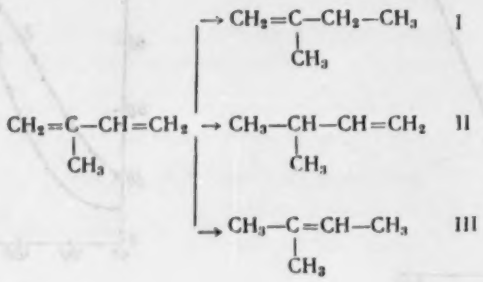
The characteristics of the fractions collected are given in the table. On the basis of the data obtained, it may be assumed that fraction I consisted of isopropylethylene. Fraction II was a mixture of isopropylethylene and unsymmetrical methylethylethylene. Fraction III was unsymmetrical methylethylethylene, fraction IV was a mixture of unsymmetrical methylethylethylene and trimethylethylene, and fraction V was trimethylethylene. The high values of the constants for fraction IV are probably due to incomplete removal of the isoprene on treatment with maleic anhydride. This is confirmed by the presence of a small plateau corresponding to the b.p. of isoprene on the distillation curve of the catalyzate.

Characteristics of Catalyzate Fractions Formed on Hydrogenation

Fraction	Boiling range, °C	Quantity		n_D^{20}	d_4^{20}	Bromine number	Olefin content, %*
		g	wt. %				
		a) Isoprene					
I	20—20,2	2,7	10	1,3682	0,6393	226	99,8
II	20,5—31,0	2,3	8	1,3736	0,6595	—	—
III	31,5—32,0	4,0	15	1,3781	0,6563	244	104
IV	32,5—38,5	4,5	17	1,3984	0,6690	—	—
V	38,5—38,6	9,8	35	1,3879	0,6599	220	99,6
	Residue	4,2	15	1,5098	—	—	—
		b) Piperylene					
I	30,6—31,8	5,8	21	1,3758	0,6443	214	98
II	32,0—35,4	4,4	15	1,3778	0,6591	218	100
III	35,6—36,6	8,8	31	1,3795	0,6542	222	102
IV	36,8—42,2	5,3	19	1,4280	0,6332	—	—
V	42.2—42,8	1,0	3	1,4332	0,6870	—	—
	Residue	3,4	11	—	—	—	—

*Calculated for pentene.

From the distillation curve (Fig. 3, Curve 1) and the properties of fraction II it follows that isopentane was not formed in the reaction. Thus isoprene is hydrogenated only to the monoolefin on zinc catalyst; hydrogen adds on in all three possible directions:



direction III predominating.

From Fig. 2 (Curve 2) it is evident that the hydrogenation of piperylene begins below 80°. The reaction goes most rapidly in the temperature interval 100-140°. At 150° the unsaturation of the catalyzate fell to 58% of the initial value, calculated for the diene. For identification of the reaction products an experiment was performed in which 34 g of piperylene was hydrogenated at an initial pressure of 100 atm. The catalyst volume was 75 ml. After removal of catalyst and drying there was obtained 28.6 g of a catalyzate with n_D^{20} 1.3824, which was fractionated in a column with an efficiency of 70 t.p. In Fig. 3 the distillation curve (2) of the catalyzate is shown, and the characteristics of the fractions collected are given in the table. The data obtained show that fraction I consisted of pentene-1, fraction II was a mixture of pentene-1 and pentene-2, and fraction III was mainly pentene-2. Fraction IV was the original piperylene with admixture of pentene-2. Fraction V was unreacted piperylene. From the properties of fractions I, II, and III it is evident that the hydrogenation of piperylene on zinc stops at the monoolefin stage. Pentene-2 predominates in the reaction products; n-pentane is not formed in the process.

Investigation of the catalyst composition by the chemical method showed that it contained about 5% aluminum. It was found by the x-ray method that it also contained zinc and aluminum oxides. However, the activity and selectivity of action of zinc catalyst are undoubtedly determined by its metallic component. This is confirmed by its high activity in the reduction of carbonyl compounds and the isomerization of allyl-type unsaturated alcohols at temperatures (of the order of 50-120°) at which zinc oxide is quite inactive in the indicated processes. Hence it must be supposed that the oxide film on the catalyst is porous and its metallic surface is accessible to the reacting components. In order to test this hypothesis we studied the change of activity of zinc catalyst with respect to styrene hydrogenation, on treatment with air. A current of air was passed over the catalyst for 0.5 hour at 250°, followed by styrene at a rate of 0.4 ml/min for 50 min. (Catalyst volume 50 ml). From Fig. 4 it is evident that after two treatments the activity of the catalyst fell to 50%, and after 2.5 hours it was completely deactivated.

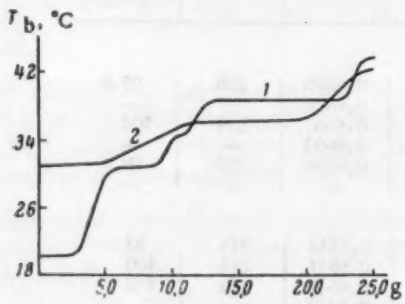


Fig. 3. Distillation curves of catalyzates obtained on hydrogenation of isoprene (1) and piperylene (2).

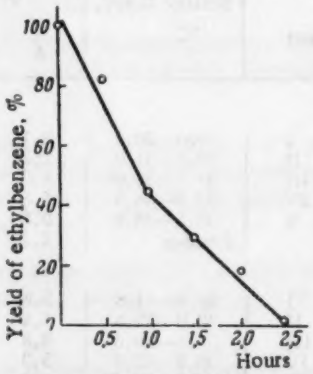


Fig. 4. Deactivation of zinc catalyst by air. Relation between the degree of hydrogenation of styrene to ethylbenzene and the time of treatment of the catalyst with air at 250°.

SUMMARY

1. It was found that skeletal zinc selectively catalyzes the hydrogenation only of ethylenic bonds activated by an adjacent phenyl group or conjugated double bond. Styrene is hydrogenated at atmospheric pressure, whereas isoprene and piperylene are hydrogenated only at elevated pressures. This makes it possible to distinguish activated double bonds from nonactivated ones, and styrene double bonds from dienic.

2. It was shown that on zinc catalyst, diene hydrocarbons with a system of conjugated double bonds are selectively hydrogenated to monoolefins. Hydrogen adds to isoprene preferentially in position 1,4, whereas it adds to piperylene at the terminal bond, which is less substituted.

3. The catalyst is deactivated by treatment with air. This indicates the metallic nature of its active surface.

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THE RELATIONSHIP BETWEEN THE ACTIVITY OF GRADE GK-1 AMMONIA CATALYST AND THE RATE OF FLOW OF GAS DURING REDUCTION

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A study has been made of the influence of the volume rate during reduction on the activity of four-times promoted industrial iron ammonia catalyst at a pressure of 300 kg/cm^2. The effect of the volume rate on the activity of the catalyst increases with decrease in the particle size, due to the difference in the conditions under which internal transfer takes place when particles of different grain size are reduced.

The formation of the active surface of iron ammonia catalysts takes place during their treatment with hydrogen, in which the iron oxides are reduced to metallic iron. Many years of plant experience and a number of special studies indicate that the activity of the catalysts depends to a great extent not only on their initial chemical composition and method of preparation, but also on the conditions under which they are reduced. The most important parameters determining the quality of the catalyst obtained are the temperature conditions and the concentration of water vapor in the reaction zone during reduction. The concentration of water vapor in the reaction zone, other conditions being equal, is usually controlled by changing the rate of flow of gas through the layer of contact catalyst being reduced.

In the study of a model catalyst consisting of thin plates of Armco iron promoted with alumina, it was found [1] that increase in the rate of flow of the nitrogen–hydrogen mixture (from 4 to 50 liter/hr) during reduction leads to a considerable increase in the activity of the catalyst throughout the whole temperature range studied (375-500°).

In a study of the influence of the volume rate in the reduction of technical iron catalysts [2-5] it was shown that decrease in the volume rate below 20000-30000 hr^{-1} usually leads to a considerable decrease in the activity of the contact catalyst, although the decrease is not so sharp as that observed in the work cited above. Recently, however, it has been suggested that if the reduction process is carried out with a sufficiently slow increase in temperature, decrease in the volume rate, even to 1000 hr^{-1}, has little effect on the activity of the contact catalyst produced [6]. This question is of considerable theoretical as well as practical interest, since the heating of large quantities of gas during the reduction of ammonia catalysts in industrial columns involves considerable difficulties and the expenditure of large quantities of energy.

We have studied the influence of the volume rate during the reduction of grade GK 1 catalyst on its activity at a pressure of 300 kg/cm^2.

Procedure and Results

A nitrogen-hydrogen mixture of stoichiometric composition, obtained by decomposition of synthetic ammonia, was purified at low pressure from traces of ammonia and water vapor and pumped by means of a five-stage compressor into a high-pressure purification system packed with active charcoal, silica gel at 100-120°, nickel catalyst, fused alkali, and alumina. A diagram of the assembly is given in Fig. 1. The purified nitrogen–hydrogen mixture, containing not more than 0.00004 g of moisture per liter, passed via a pressure-regulating valve [7] into

a buffer vessel which was connected directly to the reaction vessel. The pressure in the high-pressure purification system was kept 20-50 kg/cm² above the working pressure in the reaction vessel. At the outlet from the reaction vessel the gas mixture was reduced to atmospheric pressure and directed by means of a three-way tap either to a collector for analysis or back into the gas-holders via the cracker and high-pressure purification system.

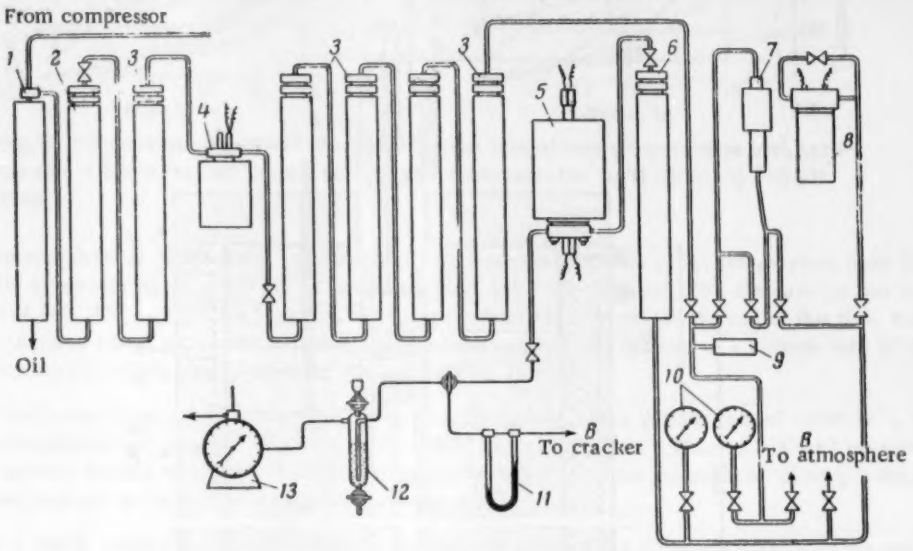

Fig. 1. Diagram of the assembly: 1) oil separator; 2) high-pressure vessel filled with active carbon; 3) high-pressure vessels filled with silica gel, fused alkali, and alumina; 4) column with nickel catalyst; 5) reaction vessel; 6) buffer vessel; 7) pressure-control valve; 8) pressure regulator; 9) safety valve; 10) manometers; 11) rheometer; 12) analysis bottle; 13) gas meter.

The reactor (Fig. 2) consisted of a high-pressure vessel with diameter 33/140 mm, prepared from grade 1Kh18N9T stainless steel. The reaction vessel contained a catalyst tube (6) with external spiral groove. The gas was introduced from below into the inner space of the reaction vessel, passed into the spiral groove on the catalyst tube, and up into the catalyst. A layer of broken quartz (8) was sprinkled between the meshes (10) and catalyst (9). The temperature was controlled by means of three chromel–alumel thermocouples (7) to within ±0.5°. The uppermost thermocouple was placed at a distance of 2-3 mm above the upper mesh and the lowest thermocouple at the same distance below the lower mesh. The third thermocouple was placed in a hole bored in the casing of the reaction vessel at the level of the catalyst layer. The first two thermocouples were fitted by means of stainless steel cones insulated from the casing of the reaction vessel by mica packing. When the exothermic reaction of ammonia synthesis was not taking place, the readings of the first and second thermocouples were identical. When the activity of the specimens was being tested at a pressure of 300 kg/cm² and high degrees of conversion, the temperature of the gas mixture leaving the gas layer was higher than that entering the layer. The difference, however, did not usually exceed 5-7°. The temperature of the gas leaving the catalyst layer was taken as the experimental temperature.

The studies were carried out with four-times promoted industrial grade GK-1 catalyst prepared in the plant in February 1959 by remelting in an electric furnace. The chemical composition of the original catalyst, its true and apparent specific gravity, and its porosity are given in the Table. For comparison, data for a twice-promoted grade A catalyst prepared in 1955 are also given.

The true specific gravity of the catalyst was determined pycnometrically by means of benzene, and the apparent specific gravity was measured in an apparatus of the Herbst type. The porosity of the unreduced catalysts was calculated from the difference between the true and apparent specific gravities.

Characteristics of Grade GK-1 and Grade A Catalysts

Catalyst	Chemical composition, %						Specific gravity, g/cm³		Porosity, %
	Fe_2O_3	FeO	Al_2O_3	K_2O	CaO	SiO_2	true	apparent	
GK-1	58,41	32,13	3,76	0,87	3,40	1,03	5,12	4,56	10,9
	64,37	29,20	3,98	2,15	—	—	5,65	4,65	17,7

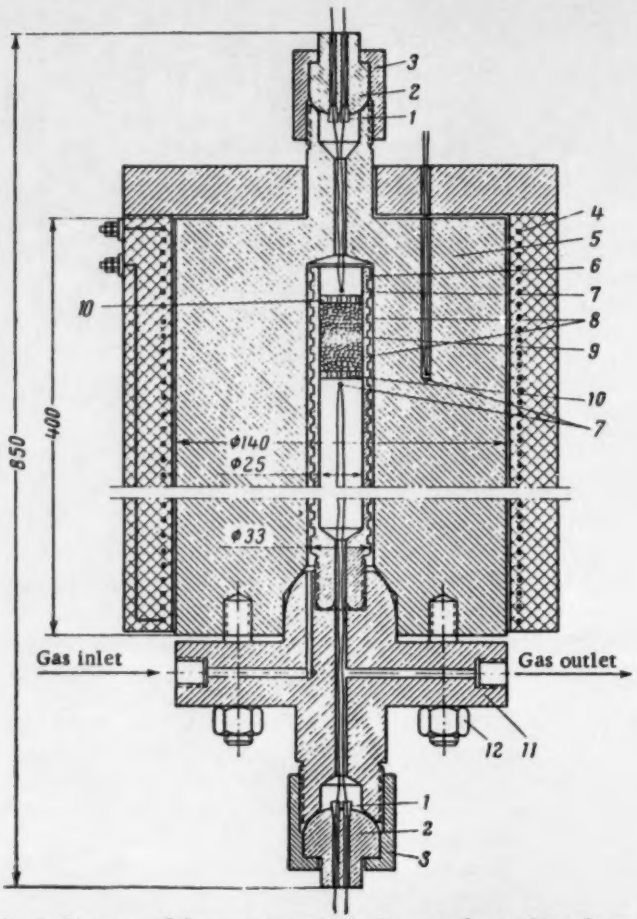

Fig. 2. Diagram of the reaction vessel: 1) cones for packing thermocouples; 2) packing heads; 3) coupling nuts; 4) electrical heating spiral; 5) reactor casing; 6) catalyst tube; 7) thermocouples; 8) quartz; 9) catalyst; 10) meshes; 11) roof of casing; 12) studs and nuts.

The experiments were carried out with catalyst specimens with two different particle sizes: 4.5 and 1.0-2.0 mm. The 4.5 mm particles were spherical. The 1.0-2.0 mm catalyst was rolled beforehand between two sheets of thick paper, after which the fines smaller than 1.0 mm were sifted out. The experiments were carried out with 2 ml of catalyst (4.980 ± 0.003 g).

The catalyst specimen was placed in the reaction vessel and reduced with the nitrogen–hydrogen mixture, which had been passed through the purification system at a pressure of 300-320 kg/cm². The reduction was carried out at atmospheric pressure under a given set of temperature conditions and at different volume rates of flow of the gas mixture leaving the reaction vessel was passed successively through two small traps immersed in liquid air and through a gas meter. The traps were changed and weighed every two hours and at the end of the experiment the ammonia which had frozen out in the traps was titrated. The studies were carried out with six catalyst

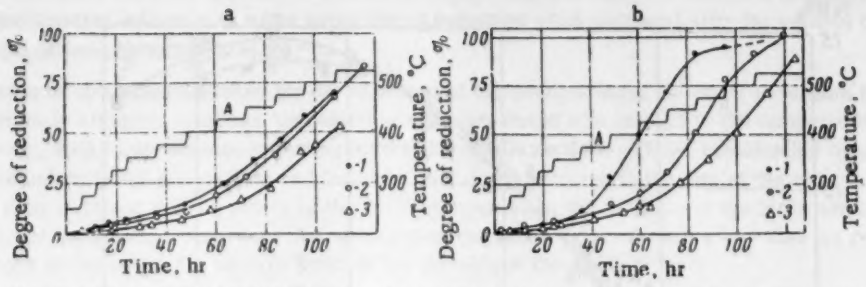

Fig. 3. Temperature conditions (A) and reduction rate of catalyst specimens with particle size 4.5 mm (a) and 1.0-2.0 mm (b) at volume rates (hr^{-1}): 1) 30000; 2) 5000; 3) 2000.

specimens at volume rates of 30000, 5000 and 2000 hr^{-1} with step-wise increase in the temperature from 250 to 500°(525°) at 25° intervals (Fig. 3, a and b). At temperatures of 250, 275, 300, and 325°, the catalyst was treated for 6 hours and at 350, 375, ..., 525° for 12 hours, including the heating-up time. At the end of this time the pressure in the reaction vessel was raised to 300 kg/cm^2 and the catalyst was reduced at a volume rate of 30000 hr^{-1} to constant activity, which usually required not less than 10-12 hours.

The catalytic activity was determined at a pressure of 300 kg/cm^2 and a volume rate of 30000 hr^{-1}. The experimental temperature was changed from 500 (525) to 300° with subsequent increase to 525° and lowering to 300°. The gas mixture leaving the reaction vessel was analyzed periodically for ammonia by passing it through a vessel containing standard sulfuric acid solution and through a gas meter.

Figure 4, a and b, compares curves showing the relationship between the ammonia content of the gas mixture leaving the reaction vessel and the temperature of the experiment for catalyst specimens with particle sizes of 1.0-2.0 and 4.5 mm.

DISCUSSION OF RESULTS

Increase in the concentration of water vapor in the reduction mixture leads to a sharp decrease in the activity of the catalyst obtained [1]. On the other hand it is known that in the reduction of technical twice-promoted catalyst, a significant influence is shown by the processes involved in the transfer of water vapor from the internal regions of the porous pieces of catalyst [8, 9]. The GK-1 catalyst which we studied has a lower porosity than the twice-promoted catalyst (see Table), so that the diffusion retardation during its reduction should have an even greater effect. Comparison of the data given in Fig. 3, a and b, shows that the rate of the reduction of the GK-1 catalyst does in fact increase appreciably with decrease in the particle size from 4.5 to 1.0-2.0 mm.

When the volume rate of flow of the gas mixture is increased, the rate of the reduction process increases, and the difference in the rates is much greater for fine catalyst particles than for coarse particles. This difference in the behavior of specimens with large and small particle sizes is also related to the influence of internal transfer processes. As a result of the diffusion retardation in the center of the piece of catalyst, there is an accumulation of considerable quantities of water vapor, which reduces the rate of the reduction process. The diffusion exchange takes place more rapidly in small particles than in large particles. As a result, the decrease in the concentration of water vapor in the gas space between the particles of the contact catalyst, which takes place when the volume rate is increased, leads to a considerable decrease in the concentration of water vapor in the pores and hence to an increase in the rate of reduction of the catalyst with small particle size. The concentration of water vapor in the center of the piece of catalyst increases considerably with increase in the particle size of the catalyst. In this case even a sharp decrease in the concentration of water vapor in the gas mixture between the catalyst particles cannot bring about a significant change in the concentration of water vapor in the interior of the pores of the catalyst particles, so that it cannot lead to a significant increase in the rate of the reduction process.

On the basis of the data obtained for the kinetics of reduction of the catalyst at different volume rates of flow of the gas mixture, it may be expected that the influence of the rate of flow on the process involved in the formation of the active catalyst surface should be shown to a greater extent for specimens with a particle size of

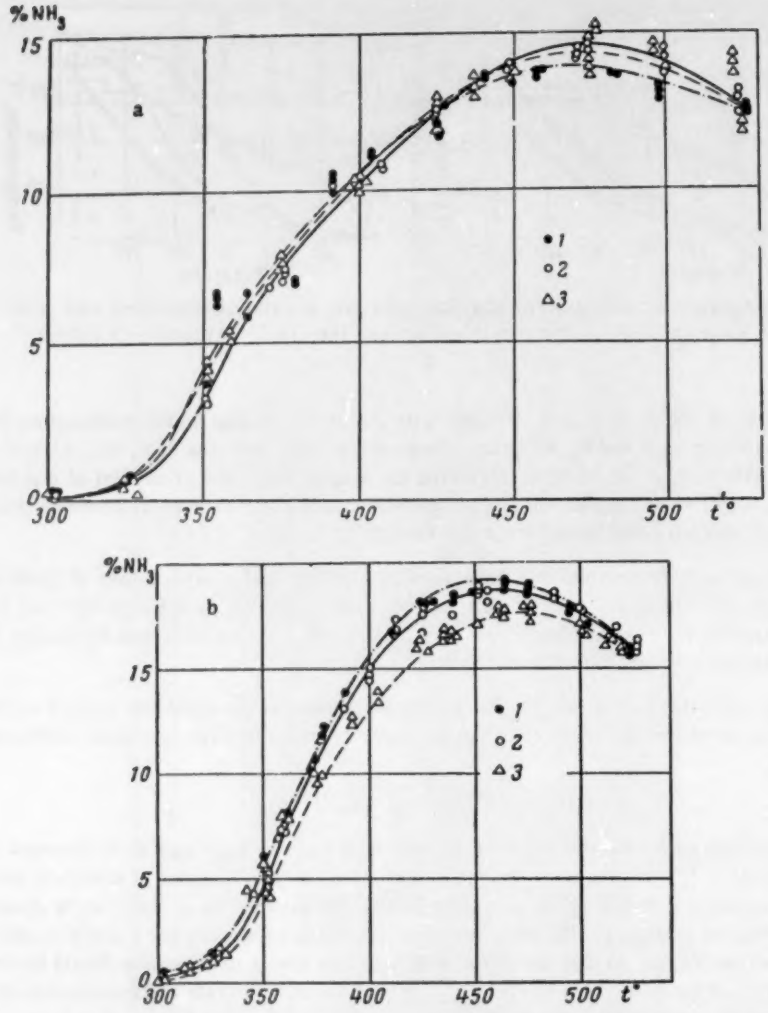

Fig. 4. Relationship between the ammonia content of the gas mixture leaving the reaction vessel and the temperature for catalyst specimens with particle size 4.5 mm (a) and 1.0-2.0 mm (b), reduced at volume rates (hr^{-1}): 1) 30000; 2) 5000; 3) 2000.

1.0-2.0 mm than for catalysts with a particle size of 4.5 mm. Figure 4 a shows that the activity of catalyst specimens with a particle size of 4.5 mm is practically independent of the volume rate during reduction. The activity of specimens with a particle size of 1.0-2.0 mm increases slightly with increase in the volume rate during reduction (Fig. 4b).

Thus the influence of the volume rate during the reduction of technical iron catalysts on their activity in ammonia synthesis is directly related to the conditions of the internal diffusion transfer of water vapor in the pores of the catalyst particles. With change in these conditions (particle size of the contact catalyst, its porosity, the temperature and pressure during reduction, the composition of the gas mixture, etc.), the influence of the volume rate during reduction may affect the activity of the catalyst to a greater or lesser extent.

The smaller the particle size of the catalyst and the greater its porosity, the sharper the increase in its activity which may be brought about by increasing the volume rate during reduction, as has been observed in a number of studies [2-5] carried out on finely divided twice-promoted catalysts.

It is not impossible, however, that the four-times promoted catalyst which we studied is in general less subject to the deactivating influence of water vapor during reduction when compared with the contact catalysts containing one [1] or two promoters [2-5].

In the choice of optimum conditions for the reduction of the catalyst under industrial conditions inside or outside the columns in ammonia synthesis, considerable attention should also be paid to the temperature conditions of the process. With rapid increase in temperature and low volume rates of flow, considerable quantities of water vapor accumulate in the gas mixture and lead to a significant decrease in the rate of the reduction process, and hence to a sharp decrease in the activity of the catalyst, even when the particles of the latter are large. Thus the volume rate and temperature conditions during reduction should be chosen in such a way that the concentration of water vapor in the outlet gas mixture remains low throughout the whole process.

The data obtained also indicate that decrease in the particle size of the catalyst in an industrial column is directly associated with a significant increase in the efficiency of unit weight of the catalyst. In the first place, increase in the particle size leads to an increase in the diffusion retardation of the process of ammonia synthesis. The efficiency of the GK-1 catalyst which we tested, like that of the twice-promoted catalysts [10, 11] increases very markedly with decrease in the particle size (compare Figs. 4 a and 4 b). On the other hand, under identical reduction conditions, the specific activity of a catalyst increases with decrease in its particle size [9, 12].

SUMMARY

1. A study has been made of the reduction of four-times promoted GK-1 catalyst with particle size 1.0-2.0 and 4.5 mm with step-wise increase in the temperature and at volume rates of 30000, 5000, and 2000 hr^{-1}; a study has also been made of the activity of these specimens in the synthesis of ammonia at a pressure of 300 kg/cm^2, volume rate 30000 hr^{-1} and temperatures from 300 to 525°.

2. The activity of specimens of particle size 1.0-2.0 mm increases with the increase in the volume rate during reduction. The activity of specimens of particle size 4.5 mm remains practically constant with analogous changes in the reduction conditions.

It has been established that the change in the activity of catalysts with change in the conditions of their reduction is determined to a considerable extent by the conditions of diffusion transfer of water vapor from the internal regions of the porous catalyst particle.

3. It has been shown that decrease in the particle size provides a basic method for increasing the efficiency of unit weight of GK-1 catalyst under industrial conditions.

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COMPARATIVE STUDY OF THE ACTIVITY OF COBALT CATALYSTS IN THE POLYMERIZATION AND HYDROPOLYMERIZATION REACTIONS OF ISOBUTYLENE

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The activity of the catalyst Co-ThO_2-kieselguhr contact, and contacts consisting of the components of this, has been studied for the polymerization and hydropolymerization reactions of isobutylene both in the absence of, and under the influence of, carbon monoxide in a flow system at 190° and atmospheric pressure. On the basis of the data obtained, conclusions have been drawn as to the parts played by the individual components of the Co-ThO_2-kieselguhr catalyst in the reactions named.

The hydrocondensation reactions of carbon monoxide with α-olefins of normal structure, and the hydropolymerization of the latter under the influence of carbon monoxide in the presence of hydrogen, take place at 190-200° and atmospheric pressure on a cobalt catalyst deposited on a carrier [1]. Red clay proves to be an effective carrier. Under these conditions, using a cobalt-clay catalyst containing the two components in the ratio 1:2, isobutylene will also undergo reaction [2-4], but this in distinction from the α-olefins of normal structure, exhibits a tendency to polymerization even in the absence of carbon monoxide and hydrogen, and shows this to a high degree in mixtures containing hydrogen only. Red clay alone is found to be a more active catalyst for the polymerization of isobutylene than the cobalt-clay contact, but in the former case, as distinct from the latter, the yield of the polymerizate is not increased by adding to the isobutylene either hydrogen or a mixture of hydrogen and carbon monoxide. On the basis of these facts, the conclusion may be drawn that the polymerization and hydropolymerization reactions of isobutylene on the cobalt-clay catalyst take place according to different mechanisms and on different active centers: the polymerization is based on the clay carrier (which has an aluminosilicate character), while the hydropolymerization is based on the cobalt. The former reaction proceeds by an ionic, and the latter by a free radical, mechanism.

It would be of interest to select a cobalt catalyst which would be inactive for the reaction of ionic polymerization of isobutylene, while being active for its hydropolymerization reaction. This phenomenon may be shown by the classical catalyst for the synthesis of hydrocarbons from carbon monoxide and hydrogen, which consists of a mixture of cobalt, thoria and kieselguhr in the ratio 100:18:100, since it is known that this reaction proceeds by a radical mechanism [5]. It might be supposed that the carrier in this catalyst, kieselguhr, would be less active than the red clay for the ionic polymerization reaction. Experiments have shown [6], however, that it is on the contrary more reactive in this reaction. This lack of correspondence has moved us to a further investigation in this field.

In the present work the relationship between the polymerization reaction of isobutylene and its hydropolymerization has been elucidated both in its binary mixtures with hydrogen, and in its ternary mixtures with hydrogen and carbon monoxide. A study has also been made of the part played by the individual components in the Co-ThO_2-kieselguhr contact in the course of the reactions. A comparative investigation has been made of the

activity of the Co-ThO_2-kieselguhr contact in these reactions, and of the activities of Co-kieselguhr and ThO_2-kieselguhr catalysts in various weight proportions.

In earlier work [7], during a comparison of the activities of Co-ThO_2-kieselguhr (100:18:100) and Co-kieselguhr (1:1) catalysts on the hydropolymerization reaction of ethylene under the influence of carbon monoxide in the presence of hydrogen, the promoter function of the thoria was discovered, which enabled it to enhance the condensation properties, and diminish the hydrogenation properties of the cobalt-kieselguhr contact.

EXPERIMENTAL

The apparatus and the procedure for conducting the experiments was not different from that described earlier [3, 8]. The following contacts were employed: 1) a series of thoria-kieselguhr mixtures (from 0:1 to 0.18:1); 2) cobalt-kieselguhr (1:1 and 1:2); 3) Co-ThO_2-kieselguhr (1:0.18:1). 30 ml of the catalyst was introduced into the glass reaction tube. Two samples (1 and 2) were usually examined for each contact. The reduction and regeneration of the cobalt-kieselguhr catalysts was performed by the use of hydrogen at 450°, while the same method was followed for the Co-ThO_2-kieselguhr catalysts at a temperature of 375°. In the synthesis of hydrocarbons from carbon monoxide and hydrogen the activity of the cobalt-kieselguhr contacts was negligible (corresponding to a contraction of gas volume of $\sim 10\%$), while that of the Co-ThO_2-kieselguhr contact was very high (175 ml per cubic meter of a mixture of carbon monoxide and hydrogen in a volume ratio of 1:2). The data concerning the activity of the cobalt contacts investigated on the hydropolymerization reaction of ethylene under the influence of carbon monoxide are in agreement with those obtained earlier [7].

The catalysts were prepared by deposition, using the method described earlier [1, 7]. The experiments were carried on for periods of from 5 to 10 hours, using atmospheric pressure and a temperature of 190°, while the volume velocity of the issuing gas was around 100 hr^{-1} in the flow system. In the prolonged experiments a liquid catalyzate tended to accumulate, and this, after drying over calcium chloride, and usually also after complete hydrogenation over a platinum-carbon catalyst was fractionated at a temperature of 135° through a column containing copper units and having an effectiveness of 40 theoretical plates; the residues from this distillation were fractionated from a Wurtz flask.

The results of experiments carried out on freshly regenerated catalyst surface are given below.

The polymerization of isobutylene

Thoria-kieselguhr contact. The addition of thorium dioxide to kieselguhr causes an abrupt reduction in the activity of this in the polymerization reaction of isobutylene (Table 1). Even the addition of 0.9% of thoria causes the yield of the liquid polymerizate to diminish from 69% to 21% of the isobutylene introduced. When 8% of thoria is used, the yield of polymerizate amounts to only 3-4%, while with 15% thoria an increase occurs to about 13%. Thus, with a thoria content of 8% the kieselguhr loses its activity almost completely for the ionic polymerization of isobutylene. Experiment shows that the catalyst Co-ThO_2-kieselguhr (100:18:100) has the optimum thoria content for the purpose of synthesizing hydrocarbons from carbon monoxide and hydrogen, and that this, containing as it does 8% thoria, is also inactive in the ionic polymerization reaction (see below). The reaction for the inactivating effect of thoria on kieselguhr in the ionic polymerization reaction probably lies in the disturbance of the acidic character of the kieselguhr, or in the formation of a new phase through the interaction of the components of the catalyst: it is a matter requiring further investigation.

Cobalt-kieselguhr contacts are considerably more active than kieselguhr itself (Table 2). On a cobalt-kieselguhr contact (1:2) the polymerization of the isobutylene proceeds less strongly than on a contact with ratio 1:1. It seems that in this case the formation of a new phase takes place owing to interaction between the components. The polymerizate obtained on the cobalt-kieselguhr contact of composition ratio 1:1 consisted of ca. 70% of dimers (of which ca. 57% was 2,4,4-trimethylpentene-1 and 2,4,4-trimethylpentene-2), and ca. 22% of trimers of isobutylene (Table 3), which points to a typical ionic polymerization of the isobutylene.

Cobalt-thoria-kieselguhr contact. This is practically inactive in the ionic polymerization reaction of isobutylene: the yield of liquid polymerizate was less than one percent of that obtained in the case of kieselguhr itself (see the data in Table 2 and the 1st experiment in Table 1). If it was shown earlier [7] that thoria in a concentration of 8% diminishes the hydrogenating activity and increases the condensing activity of cobalt-kieselguhr

TABLE 1

Polymerization of Isobutylene on Thoria-Kieselguhr Contacts

Sample number	Wt. ratio of thoria to kieselguhr in the contacts	Gas contraction %	Yield of liquid hydrocarbons in % of the isobutylene	
			introduced	undergoing reaction
1	0 : 1	72,0	69,0	95,0
1	0,009 : 1	28,0	21,2	76,0
1	0,08 : 1	21,4	13,9	64,0
2	0,08 : 1	14,8	10,2	68,6
1	0,09 : 1	7,2	2,7	37,8
2	0,09 : 1	10,3	3,9	35,9
1	0,18 : 1	15,7	13,1	83,5
2	0,18 : 1	18,6	12,7	68,4

Note: before the experiments, each catalyst was treated with hydrogen at 400° for 4 hours.

TABLE 2

Polymerization of Isobutylene on Cobalt-Kieselguhr Contacts

Sample number	Composition of catalyst	Gas contraction, %	Yield of liquid hydrocarbons in % of the isobutylene	
			introduced	undergoing reaction
1	Co-Kieselguhr (1:1)	37.4	24.4	65.5
1	Co-Kieselguhr (1:2)	17.9	6.2	34.2
1	Co-ThO_2-Kieselguhr (100:18:100)	3.9	0.5	13.3
2	The same	3.3	0.7	21.5

contacts with ratio 1:1 in the hydrocondensation of carbon monoxide with ethylene, then the current work has shown that 8% of thoria is also effective in producing the complete inactivation of the catalyst for the purpose of ionic polymerization. It is known that 8% of thoria (0.18 part per part of cobalt) represents the optimum concentration for the purpose of hydrocarbon synthesis from carbon monoxide and hydrogen. Thus, the effect of thoria on the catalytic properties of the cobalt-kieselguhr contact appears to be of more than one kind.

It follows from the results which have been obtained that the polymerization of isobutylene is accomplished by the kieselguhr, and so, apparently, possesses ionic character. The addition of cobalt or thoria causes strong inactivation, and their simultaneous addition causes complete inactivation of the kieselguhr with respect to this reaction. This is in agreement with the data obtained earlier [3] in similar experiments using clay, and cobalt-clay mixtures, as catalysts. It may be supposed that the role of thorium dioxide in the promoting of cobalt catalysts for the synthesis of hydrocarbons from carbon monoxide and hydrogen consists to a significant degree in its power to cause loss of activity with respect to the polymerization by an ionic mechanism.

TABLE 3

Fractions of the Catalyzate obtained from Isobutylene on a Cobalt-Kieselguhr Contact of Composition Ratio 1:1

Boiling range, °C	Yield of fraction, vol., %	d_4^{20}	n_D^{20}	Hydrocarbons
98—101	4,9	—	1,4080	
101—102	38,8	0,7130	1,4098	2,4,4,-trimethylpentene-1 and
102—104	12,3	0,7173	1,4125	2,4,4-trimethylpentene-2
104—106	6,3	0,7194	1,4147	
106—134	11,4	1,7311	1,4220	
134—191	22,2	0,7633	1,4336	Trimers of isobutylene
Residue and loss	4,1			
Emergent catalyzate	100	0,7279	1,4181	

TABLE 4

Hydropolymerization of Isobutylene on Cobalt-Kieselguhr Contacts

Sample Number	Composition of catalyst	Ratio of isobutylene to hydrogen in the emergent	Gas contraction, %	Yield of liquid hydrocarbons in % of the isobutylene		Amount undergoing reaction %	
				introduced	undergoing reaction	isobutylene	hydrogen
1	Co-kieselguhr (1:1)	1 : 1	64,0	18,0	20,4	86,9	84,0
1	Co-kieselguhr (1:2)	1 : 1	55,6	5,3	5,9	90,5	75,0
2	The same	1 : 0,9	34,7	5,2	7,2	71,5	73,0
1	Co-ThO_2-kieselguhr (100:18:100)	1 : 1	53,2	5,3	6,1	87,6	87,0

The hydropolymerization of isobutylene (mixed with hydrogen, but in the absence of carbon monoxide)

Cobalt-kieselguhr contacts (Table 4). On a cobalt-kieselguhr contact (ratio 1:1), the yield of liquid catalyzate, based on the isobutylene introduced (18%), arising from an equivalent mixture of isobutylene and hydrogen, is appreciably lower than the yield obtained in the polymerization of isobutylene alone (Table 2). On a cobalt-kieselguhr contact (ratio 1:2), however, the yield (6%) is about the same as that obtained from pure isobutylene. Thus, in the absence of a cobalt-clay contact [3], addition of hydrogen to the isobutylene does not increase the yield of the liquid hydropolymerizate on cobalt-kieselguhr contacts. It is possible that, under these conditions, the components of the catalyst enter into mutual interaction, forming a new phase which is inactive in promoting hydropolymerization, though it is still active in promoting the direct polymerization of the isobutylene. There are indications in the literature of the possibility of interaction between the cobalt component and kieselguhr [9, 10].

In the presence of the Co-ThO_2-kieselguhr contact, the yield of liquid product from an equivalent mixture of isobutylene and hydrogen is ten times higher than that obtained from isobutylene alone. It is possible that this points to the hydropolymerization of isobutylene having a nonionic nature. Intense hydrogenation has been observed on all the cobalt catalysts: hydrogen entered into reaction to the extent of 75-87%, gas contraction amounted to 53-64%, and the yield of liquid hydropolymerizate based on the isobutylene entering into reaction amounted to between 6 and 20%.

Hydropolymerization of isobutylene under the influence of carbon monoxide

Cobalt-kieselguhr contacts (Table 5). The addition of carbon monoxide to an equivalent mixture of isobutylene and hydrogen leads to an increase in the yield of hydropolymerizate based on the isobutylene introduced by about a factor of 2. The yield based on the isobutylene entering into reaction is also increased several fold. Change of carbon monoxide concentration in the initial gas from 0.6% to 10% has only a slight effect on the yield of hydropolymerizate, in contrast with the effect on the cobalt clay contact (ratio 1:1) [3,4], for which the yield of hydropolymerizate on the basis of the initial isobutylene is increased by a factor of 3 (from 18% to 60%) on addition of 5% carbon monoxide, and then slowly decreases with further increase in the carbon monoxide content. With increase of the carbon monoxide in the initial gas in the case of the cobalt-kieselguhr contacts, the proportions of the isobutylene, carbon monoxide and hydrogen which undergo reaction are reduced (see Figure), which may be partially explained by the reduction in the hydrogenation reaction.

The catalyzate ($d^{20}_4 = 0.6933$, $n^{20}_D = 1.4089$, bromine number = 130.5) obtained in the course of a prolonged experiment on a cobalt-kieselguhr contact (ratio 1:1) using an equivalent mixture of isobutylene and hydrogen + 5% carbon monoxide, was hydrogenated, and the 34 ml hydrogenizate obtained was submitted to distillation through a column (Table 6). It contained ca. 12% of C_5 and C_6 hydrocarbons ca. 12% of n-heptane 26% of 2,2,-4-trimethylpentane, 20% of other octane isomers, and ca. 22% of hydrogenated trimers of isobutylene. The published data [11] for n-heptane are: b.p. 98.43°, $d^{20}_4 = 0.6837$, $n^{20}_D = 1.3877$; while those for 2,2,4-trimethylpentane are: b.p. 99.24°, $d^{20}_4 = 0.6919$, $n^{20}_D = 1.3915$. In the presence of the cobalt-clay catalyst (ratio 1:2), a gas of the same composition (1:1 with respect to isobutylene and hydrogen, + 5% carbon monoxide), under the same conditions, gave a hydropolymerizate which, after complete hydrogenation, consisted exclusively of 2-methylalkanes [12].

TABLE 5

Experiments Using Ternary Mixtures of Isobutylene, Hydrogen and Carbon Monoxide in the Presence of Cobalt-Kieselguhr Contacts

Sample number	% CO in initial gas	Ratio $CO:H_2$: iso-C_4H_8 in the initial gas	Gas contraction %	Yield of liquid catalyzate in % of the isobutylene introduced	Yield of liquid catalyzate in % of the isobutylene undergoing reaction	Amount undergoing reaction %: iso-C_4H_8	CO	H_2
			Cobalt-kieselguhr					
1	4,6	1 : 9,9 : 10,6	72,0	34,4	50,5	68,0	99,0	96,4
1	10,0	1 : 4,3 : 4,6	52,0	27,9	43,0	67,6	56,5	57,4
1	9,0	1 : 4,9 : 5,0	66,6	36.8	57,0	64,0	80,0	78,0
			Cobalt-kieselguhr					
1	0,6	1 : 84,6 : 79,0	46,0	10,7	14,2	74,0	65,0	55,5
2	4,0	1 : 12,1 : 11,1	46,6	13,4	24,4	55,0	84,0	72,8
1	5,0	1 : 9,6 : 9,0	40,0	11,2	23,5	47,5	30,2	49,0
1	9,0	1 : 4,8 : 5,2	21,5	11,3	29,1	39,0	6,7	14,1

TABLE 6

Fractions of Hydrogenated Catalyzate, Obtained from a 1:1 Mixture of Isobutylene and Hydrogen containing 5% Carbon Monoxide on a Cobalt-Kieselguhr contact of ratio 1:1

Boiling point limits °C	Yield of fraction, vol. %	d^{20}_4	n^{20}_D	Hydrocarbons
43-87	11.8	0.6463	1.3720	C_6
87-98	11.8	0.6821	1.3880	n-heptane
98-99.6	25.9	0.6920	1.3920	2,2,4-trimethylpentane
102-107	4.7	—	1.4020	C_8
109 120	15.3	0.7202	1.4105	C_8
130-194	22.4	0.7609	1.4210	Hydrogenated trimers of isobutylene
Residue and loss	9.1			
Initial hydrogenizate	100	0.6989	1.4040	

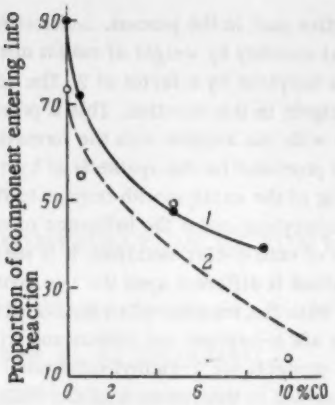
The catalyzate (d^{20}_4 = 0.7073, n^{20}_D = 1.4149, bromine number = 164.7) obtained by the use of a cobalt-kieselguhr (ratio 1:1) contact from an equivalent mixture of isobutylene and hydrogen + 10% carbon monoxide was completely hydrogenated and fractionated through a column. The 33 ml used gave results shown in Table 7. The results obtained lie close to the data contained in Table 6. On a cobalt-clay catalyst (ratio 1:2) [3], an initial equivalent mixture of hydrogen and isobutylene containing 7% of carbon monoxide gave a catalyzate which after hydrogenation also consisted principally of n-pentane and 2,2,4-trimethylpentane.

TABLE 7

Fractions of Hydrogenated Catalyzate, Obtained from a 1:1 Mixture of Isobutylene and Hydrogen Containing 10% Carbon Monoxide on a Cobalt-Kieselguhr Contact of ratio 1:1

Boiling point limits,°C	Yield of fraction, vol.%	d^{20}_4	n^{20}_D	Hydrocarbons
65.5-97.5	15.3	0.6674	1.3840	C_6
98-99	9.7	0.6881	1.3910	2,2,4-trimethylpentane with impurity of n-heptane
99-100	22.0	0.6899	1.3915	2,2,4-trimethylpentane
100-110	12.2	0.6984	1.3958	C_8
110-124	12.8	0.7132	1.4040	C_8
135-195	22.6	0.7529	1.4270	Hydrogenated trimers of isobutylene
Residue and loss	5.4			
Initial hydrogenizate	100	0.7016	1.4004	

On a Co-ThO_2-kieselguhr contact addition of carbon monoxide to an approximately equivalent mixture of isobutylene and hydrogen results in an increase in the yield of liquid hydrocarbons some two or three fold, when expressed as a percent of the isobutylene introduced (Table 8). Variation in the carbon monoxide content in the



Relationship between the proportion of isobutylene entering into reaction (1), and the proportion of hydrogen entering into reaction (2) and the carbon monoxide content of the initial gas on a cobalt-kieselguhr catalyst of ratio 1:2.

initial gas has no effect on the yield of liquid products in terms of percent of the isobutylene introduced, but, in contrast with the experiments on cobalt-kieselguhr contacts, it has also only a small influence on the proportions of hydrogen and carbon monoxide undergoing reaction. The proportion of isobutylene entering into reaction, however, diminishes with increase in the carbon monoxide concentration in the initial gas. Thus, an increase in the carbon monoxide content from 1% to 20% causes the proportion of butylene reacting to go down from 84% to 11.8%, while the proportion of hydrogen reacting changes only from 89.4% to 76.0%. This is explained by supposing that increase in the carbon monoxide concentration in the initial gas enhances the reaction producing hydrocarbons from carbon monoxide and hydrogen at the expense of the hydropolymerization of the isobutylene. This explanation also covers the fact that when the carbon monoxide content in the initial gas is 18-20%, the yield of liquid products, calculated on the basis of the isobutylene undergoing reaction, amounts to around 130%. The liquid catalyzate obtained in the presence of the Co-ThO_2-kieselguhr catalyst is different in composition from the hydropolymerizate obtained on the cobalt-kieselguhr contact not promoted by the presence of thorium dioxide. The catalyzate ($d^{20}_4 = 0.6749$, $n^{20}_D = 1.4091$, bromine number = = 79.5) obtained on the Co-ThO_2-kieselguhr catalyst contact from an equivalent mixture of isobutylene and hydrogen containing 5% of carbon monoxide was, in a quantity of 16 ml, distilled through a column, and the results obtained are given in Table 9. The composition of this catalyzate was different from that of the catalyzate obtained from a similar gas mixture on a cobalt-kieselguhr catalyst: there was a predominance of little-branched hydrocarbons in it, while dimers and trimers did not make up an appreciable part.

TABLE 8

Experiments with Ternary Mixtures of Isobutylene Hydrogen and Carbon Monoxide, in the Presence of Co-ThO_2-Kieselguhr Catalysts of ratio 100:18:100

Sample number	% CO in initial gas	Ratio CO:H_2: iso-C_4H_8 in initial gas	Gas contraction %	Yield of liquid catalyzate in % of isobutylene		Amount undergoing reaction %		
				introduced	undergoing reaction	iso-butylene	CO	H_2
1	1,0	1 : 53,4 : 41,5	53,6	10,1	12,1	84,0	100	89,4
1	3,0	1 : 16,5 : 15,6	53,5	10,8	15,8	69,0	79,0	98,5
2	4,0	1 : 9,2 : 14,5	43,8	13,5	29,6	46,0	93,5	83,0
1	5,0	1 : 9,3 : 9,7	45,9	11,4	24,6	45,8	84,4	71,3
1	5,6	1 : 9,2 : 7,8	51,0	17,6	36,7	43,4	95,0	93,4
1	10,0	1 : 4,6 : 4,2	49,5	—	—	30,2	91,0	77,0
1	20,0	1 : 2,2 : 1,7	50,6	15,5	133	11,8	87,6	76,0

TABLE 9

Fractions of the Catalyzate Obtained from a 1:1 mixture of Isobutylene and Hydrogen Containing 5% Carbon Monoxide on a Co-ThO_2-Kieselguhr Contact

Boiling limits of the fraction, °C	Yield of the fraction, %	d^{20}_4	n^{20}_D	Hydrocarbons
26,5—50	15,8	0,6272	1,3650	C_5
50—74	17,7	0,6545	1,3756	C_6
76,5—100	13,9	0,6801	1,3890	C_7
104—125	11,4	0,7034	1,3990	C_8
145—295	37,2	0,7635	1,4302	—
Residue and loss	4,0			

The results obtained in this work show that kieselguhr takes an active part in the process, facilitating the polymerization of the isobutylene. Addition to the kieselguhr of an equal quantity by weight of cobalt diminishes the catalytic activity of this promoter of the ionic polymerization of the butylene by a factor of 2. The addition of 8% of thoria leads to a practically complete inactivation of the kieselguhr in this reaction. This is presumably to be explained by the fact that the components of the catalyst interact with one another with the formation of a new phase. There thus arises a new function of the thoria as a catalyst promotor for the synthesis of hydrocarbons from carbon monoxide and hydrogen, as a consequence of its inactivating of the catalyst with respect to the ionic polymerization. By comparing the data on the hydropolymerization of isobutylene under the influence of carbon monoxide in the presence of cobalt-kieselguhr with that in the presence of cobalt-clay catalysts, it is seen that the direction of the reactions, and the nature of the liquid products obtained is different upon the two contacts. In the presence of cobalt-kieselguhr catalysts, the basic liquid products from the reaction of an equivalent mixture of isobutylene and hydrogen in the presence of 5% carbon monoxide are n-heptane and dimers and trimers of isobutylene; while on cobalt-clay catalysts under similar conditions the products are 2-methyl-substituted alkanes and the corresponding alkenes. Little-branched hydrocarbons are also obtained in the presence of Co-ThO_2-kieselguhr contact with ratio 100:18:100. The yield of liquid hydrocarbons depends only slightly on the concentration of carbon monoxide in the initial gaseous mixture in the case of the cobalt-kieselguhr contacts, and has a sharp maximum at 4-5% carbon monoxide on cobalt-clay catalyst. It seems that a radical-chain process takes place on the cobalt-clay catalyst, while on the cobalt-kieselguhr catalysis there also takes place simultaneously the ionic polymerization of isobutylene and the radical synthesis of hydrocarbons from carbon monoxide and hydrogen.

SUMMARY

1. A comparative study has been made of the activity of cobalt-thoria-kieselguhr contact, and of contacts consisting of the components of this, in the polymerization and hydropolymerization reactions of isobutylene.

2. The polymerization of isobutylene is performed on the kieselguhr and possesses an ionic character.

3. The addition of carbon monoxide or thoria has a strong inactivating effect, and simultaneous addition of both these components completely inactivates the kieselguhr with respect to the ionic polymerization reaction of isobutylene.

4. The hydropolymerization of isobutylene in the presence of cobalt-kieselguhr contacts is accompanied by the ionic polymerization of the isobutylene and the radical synthesis of hydrocarbons from carbon monoxide and hydrogen.

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All abbreviations of periodicals in the above bibliography are letter-by-letter transliterations of the abbreviations as given in the original Russian journal. *Some or all of this periodical literature may well be available in English translation.* A complete list of the cover-to-cover English translations appears at the back of this issue.

* In Russian.

THE ISOMERIZATION OF SOME HEXENES OVER CALCIUM AMIDE

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An investigation has been made of the relative rates of transfer of the multiple bonds in hexene-1, 2-methylpentene-1, 3-methylpentene-1, 4-methylpentene-1 and 2,3-dimethylbutene-1.

It has been shown that 2,3-dimethylbutene-1 and 3-methylpentene-1 undergo isomerization somewhat more difficultly than the remaining hexenes, which serves to confirm the mechanism suggested earlier for the transfer of multiple bonds in the presence of alkaline catalysts through the intermediate formation of a carbanion.

The transfer of multiple bonds in olefins is catalyzed by many substances, amongst which we may single out those possessing acidic or basic properties. Acid-base interaction occurs between such catalysts and the olefins, which results in the formation of an intermediate carbonium ion in the presence of acid catalysts [1-2], or carbanion ion in the presence of basic catalysts [3,4].

Since the mechanisms of these reactions are different, it follows that a single olefin may, in the presence of different catalysts, behave in different ways, and the elucidation of the laws governing the behavior of such systems would presumably lead to the possibility of choosing catalysts appropriate for carrying out the reaction with olefins of definite structure.

We have earlier investigated the transfer of double bonds in the presence of an oxidic catalyst, aluminum oxide, for five hexenes: hexene-1, 2-methylpentene-1, 3-methylpentene-1, 4-methylpentene-1 and 2,3-dimethylbutene-1 at 80° [5].

It has been shown that 2-methylpentene-1 and 2,3-dimethylbutene-1, distinction from the remaining hexenes, are very easily isomerized, which is explained by the presence in them of methyl groups adjacent to the double bond, these groups possessing electron donating properties, so facilitating the attachment of a proton to the olefin, with the consequent formation of the carbonium ion.

This reaction is studied in the present communication in the presence of an alkaline catalyst (calcium amide) using the same hexenes and the same temperature as in the previous work, though the rate of addition was different.

Table 1 gives the results obtained for aluminum oxide and calcium amide.

It can be seen from the data of Table 1 that, in the presence of calcium amide, 2,3-dimethylbutene-1 and 3-methylpentene-1 undergo isomerization somewhat more difficultly (54 and 50%) than the other three hexenes (70, 73 and 96%).

These data are in agreement with the mechanism suggested earlier for the transfer of multiple bonds in

TABLE 1

Isomerization of Various Hexenes in the Presence of Calcium Amide and of Aluminum Oxide

Initial diene***	Equilibrium concentration of the isomeric hexenes at 80°*	$Ca(NH_2)_2$		Al_2O_3	
		a**	b**	a	b
2,3-dimethylbutene-1	77	42	54	49	63
3-methylpentene-1	99	50	50	0	0
2-methylpentene-1	84	59	70	62	74
4-methylpentene-1	99	73	73	0	0
Hexene-1	98	95	96	0	0

*Calculated according to the formula adduced by Korobov and Frost [6]. The free energy of formation of the olefins has been taken from Rossini's reference book [7].

**a is the composition of the isomeric hexenes in the catalyzate in wt.%; b is the degree of isomerization in wt.% recalculated on the basis of the equilibrium concentration of the isomeric hexenes.

***So the Russian table reads. But there has been no mention of dienes in the text, and this must be construed as a slip. Read "hexene" or "olefin"—Translator.

olefins through the intermediate formation of carbanions [3,4] through the removal (or some shift) of a proton from the allyl position. Actually, the mobility of the allyl hydrogen is reduced as we move from the methyl group through the methylene to the methine: $CH_3 > CH_2 > CH$ [8,9] and consequently 2,3-dimethylbutene-1 and 3-methylpentene-1, which have an allyl hydrogen in the CH group, undergo isomerization more difficultly than 2-methylpentene-1, 4-methylpentene-1 and hexene-1, which have their allyl hydrogen in the CH_2 group.

Comparison of the results obtained for calcium amide with those for aluminum oxide shows that in the case of the aluminum oxide the effect of the olefin structure is incomparably greater than in the case of the calcium amide. This must presumably be regarded as due to the fact that the ionic character of the reaction is less strongly expressed in the latter case.

EXPERIMENTAL

The initial hexenes* are characterized by the following data:

hexene-1	b.p. 63.5°	$n^{20}D$	1.3880	d^{20}_4	0.6731
2-methylpentene-1	62.2°		1.3922		0.6800
3-methylpentene-1	54.2°		1.3848		0.6673
4-methylpentene-1	53.8°		1.3830		0.6641
2,3-dimethylbutene-1	55.7°		1.3907		0.6778

Method of conducting the experiments

The isomerization was carried out in a flow system at 80° with a volume velocity of 0.6 hr^{-1} over freshly prepared calcium amide [10]. The activity of the catalyst, as determined from the degree of conversion of 2-methylbutene-1, was the same for all the experiments. For the isomerization, 80 ml of each of the hydrocarbons was taken, together with 60 ml of the catalyst, and after removal of the first and second fraction distillation was carried out through a column of 80 theoretical plates. The residue of the substance retained in the structure of the column was about 1 ml. The residue was distilled from a flask. The density and refractive index was determined for each of the fractions and the residue.

*Here the Russian text contains "hexanes", the opposite error to that noted in Table 1. There is no doubt that "hexenes" is intended—Translator.

TABLE 2

Constants for the Various Isomeric Hexenes [7]

Olefin	B.p. °C at 760 mm	n_D^{20}	d_4^{20}
hexene-2-cis	68.84	1.3977	0.6869
hexene-2-trans	67.87	1.3935	0.6784
hexene-3-cis	66.44	1.3947	0.6796
hexene-3-trans	67.08	1.3943	0.6772
4-methylpentene-2-cis	56.30	1.3880	0.6690
4-methylpentene-2-trans	58.55	1.3889	0.6686
2-methylpentene-2	67.29	1.4004	0.6863
3-methylpentene-2-cis	70.45	1.4045	0.6986
3-methylpentene-2-trans	67.63	1.4016	0.6942
2,3-dimethylbutene-2	73.21	1.4122	0.7080

Table 2 gives the constants of the hexenes with the more deep-seated position of the double bond, which may be formed by the displacement of this bond in the initial olefins.

Isomerization of 2,3-dimethylbutene-1*

The distillation curve is given in Fig. 1, and the characteristics of the fractions obtained in Table 3.

TABLE 3

Fractional Composition of the Catalyzate from 2,3-Dimethylbutene-1

Fraction	B.p. °C at 760 mm	Quantity, g	n_D^{20}	d_4^{20}
1	55,2—55,7	21,3	1,3907	0,6777
2	55,8—72,4	3,3	1,3992	0,6892
3	72,5—73,2	4,0	1,4123	0,7079
4	73,2	9,3	1,4126	0,7084
Residue		1,7	1,4130	0,7088

Comparison of the properties of the fractions in Table 3 with those of the initial 2,3-dimethylbutene-1 and the properties of the isomeric hexenes given in Table 2 shows that the 1st fraction consists of 2,3-dimethylbutene-1, while fractions 3 and 4 and the residue, and therefore also the substance remaining in the still, consist of 2,3-dimethylbutene-2. Calculation of the composition of the catalyzate gave the following results: 2,3-dimethylbutene-1 ,58%, 2,3-dimethylbutene-2, 42%.

Isomerization of 3-methylpentene-1

The curve for the distillation is given in Fig. 1, and the properties of the fractions in Table 4.

Analysis of the distillation curves, and also comparison of the constants of the fractions in Table 4 with those of the expected isomeric hexenes shows that fraction 1 consists of the initial 3-methylpentene-1. Fraction 2 is a mixture of the initial hexene with trans-3-methylpentene-2. Fraction 3 consists basically of trans-3-methylpentene-2. Fraction 4 consists of a mixture of cis-and trans -3- methylpentene-2; fraction 5 and the residue are close to the properties of cis-3-methylpentene-2.

The catalyzate therefore can be estimated to consist of 50% 3-methylpentene-1, 22% trans-3-methylpentene-2, and 28% of cis-trimethylpentene-2.

Isomerization of 2-methylpentene-1

The distillation curve is given in Fig. 2, and the characteristics of the fractions in Table 5.

* The isomerization of 2,3-dimethylbutene-1 has been investigated earlier by us [3], but it seems that we were then working with an amide sample which had lost its activity.

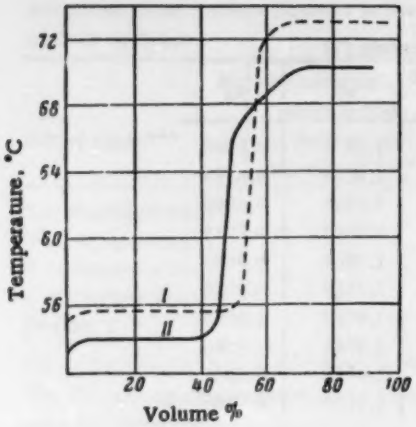

Fig. 1. Curves for the distillation of the products of the isomerization of (I) 2,3-dimethylbutene-1 and (II) 3-methylpentene-1.

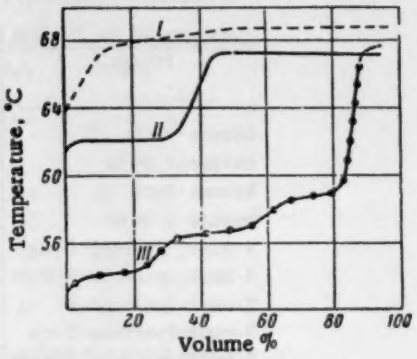

Fig. 2. Curves for the distillation of the products of the isomerization of (I) hexene-1; (II) 2-methylpentene-1; (III) 4-methylpentene-1..

TABLE 4

Fractional Composition of the Catalyzate from 3-Methylpentene-1

Fraction	B.p. °C at 760 mm	Quantity, g	n_D^{20}	d_4^{20}
1	53,7—54,2	14,7	1,3846	0,6673
2	54,3—67,4	3,3	1,3940	0,6818
3	67,5—68,7	1,9	1,4020	0,6931
4	68,8—70,1	2,6	1,4031	0,6962
5	70,2—70,3	8,8	1,4050	0,6977
Residue		1,0	1,4059	0,6992

TABLE 5

Fractional Composition of the Catalyzate from 2-Methylpentene-1

Fraction	B.p. °C at 760 mm	Quantity, g	n_D^{20}	d_4^{20}
1	61,8—62,3	13,9	1,3922	0,6800
2	62,4—67,1	4,2	1,3970	0,6831
3	67,1—67,2	14,6	1,4005	0,6864
Residue		6,0	1,4010	0,6866

In Table 5, fraction 1 consists of 2-methylpentene-1. Fraction 3 and the residue consist of 2-methylpentene-2. Fraction 2 is a mixture of these two isomers. The composition of the catalyzate is: 41% of 2-methylpentene-1; 59% of 2-methylpentene-2.

Isomerization of 4-methylpentene-1

The distillation curve is given in Fig. 2, and the characteristics of the fractions in Table 6.

In Table 6, fraction 1 contains the initial 4-methylpentene-1. Fraction 3 is close to the properties of cis-4-methylpentene-2. Fraction 5 is trans-4-methylpentene-2. Fraction 6 contains a certain quantity of 2-methylpentene-2, and fractions 2 and 4 are of intermediate compositions.

Calculation on the basis of the data in Table 6 and the distillation curve give the following composition for the catalyzate: 27% of 4-methylpenten-1; 60% of 4-methylpentene-2; and 13% of 2-methylpentene-2.

TABLE 6

Fractional Composition of the Catalyzate from 4-methylpentene-1

Fraction	B.p. °C at 760 mm	Quantity, g	n_D^{20}	d_4^{20}
1	53,7—54,3	8,4	1,3835	0,6640
2	54,4—56,1	4,7	1,3858	0,6669
3	56,2—56,8	7,8	1,3882	0,6692
4	56,6—58,5	6,1	1,3890	0,6696
5	58,9—58,7	5,5	1,3892	0,6685
6	58,8—67,2	3,4	2,3956	0,6812
Residue		2,4	1,4040	0,6963

Isomerization of hexene-1

The distillation curve is given in Fig. 2, and the constants of the fractions obtained are given in Table 7.

In Table 7, fraction 1 consists of a mixture of the initial hexene-1 with the isomeric n-hexenes. Fraction 3 is close to the properties of cis-hexene-2.

The quantity of hexene-1 in the catalyzate does not exceed 5%, and the remaining 95% of the catalyzate consists of hexene-2 and hexene-3.

TABLE 7

Fractional Composition of the Catalyzate from Hexene-1

Fraction	B.p. °C at 760 mm	Quantity, g	n_D^{20}	d_4^{20}
1	64,1—66,9	3,4	1,3905	0,6751
2	67,0—68,7	14,6	1,3950	0,6799
3	68,8—68,9	14,3	1,3971	0,6864
Residue		5,8	1,3988	0,6872

SUMMARY

1. The relative rates of transfer of multiple bonds in hexenes containing the double bond in the α-position have been studied, using calcium amide as the catalyst.

2. The results obtained confirm the suggestion previously made concerning the mechanism of this reaction, that it proceeds through the formation of an intermediate carbanion.

3. Comparison of the relative rates of isomerization of the hexenes in the presence of aluminum oxide and in the presence of calcium amide shows that, in the latter case, the structure of the olefin exerts a smaller influence on the rate of the isomerization than in the former.

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A STUDY OF THE ORTHO-, PARA-HYDROGEN CONVERSION ON SOLID CATALYSTS

II. CATALYSIS BY THE RARE EARTH ELEMENT HYDROXIDES

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A study has been made of the catalytic activity of the hydroxides of the trivalent ions of praseodymium, gadolinium, terbium and dysprosium in relation to the ortho-, para-hydrogen conversion at 78, 64 and 22° K in the pressure range 3 to 150 atm.

The relation between the rate constant of this reaction on these hydroxides and the temperature and effective magnetic moment has been determined.

A comparison has been made of the catalytic properties of the hydroxides of elements in different groups of the periodic table.

Selection and Preparation of Hydroxide Samples. Experimental Methods and Conditions

It had previously been found [1] that the hydroxides of a series of paramagnetic ions possessed considerable catalytic activity in the low temperature ortho-, para-hydrogen conversion. In selecting ions for the preparation of the catalysts in this work we assumed that Wigner's theory [2], which was proposed for catalysts homogeneous with respect to paramagnetic ions, could also be applied, with certain approximations, to the case of heterogeneous catalysis on catalysts with sufficient magnetic dilution of the ions.

In accordance with this theory the probability of conversion, or the value of the rate constant k' for conversion, is determined by the magnitude of the effective magnetic moment μ_{eff} of the paramagnetic ion of the catalyst and by the nearest distance between it and a molecule of hydrogen during their effective impact, i.e.

$$k' \sim \frac{2\mu_{eff}^2 \mu_p^2 I}{9h^2 r^6 (kT)}.$$

Here μ_p is the magnetic moment of a proton; I is the moment of the inert molecule and h and k are universal constants.

In the two previous communications [1] it was shown that this correlation was observed satisfactorily for the iron group of elements with unfilled 3d electron shells. The maximum value of μ_{eff} for ions of this group was 5.92 (Fe^{+++}, Mn^{++}). Some of the rare earth element ions with an unfilled 4f electron shell had a μ_{eff} value of 10.6 (Dy^{+++}, Ho^{+++}).

In the light of this it seemed of interest to determine the catalytic activity of their hydroxides. Comparison of k'/μ^2_{eff} for these two groups should confirm the inverse relation between k' and r^6.

For this determination of the catalytic activity of ions with an incomplete 4f electron shell we chose the hydroxides of the trivalent ions of praseodymium, gadolinium, terbium and dysprosium.

The hydroxides were prepared by slow precipitation of the corresponding ions from their nitrate solutions by a weak alkaline solution. The precipitate was washed by decantation with distilled water, filtered, washed, dried at 40 °C and then heated in air at 100°C.

The lumps of hydroxide so-obtained were ground up into particles with 0.7-1.0 mm diameter, and the activity was determined for a fraction of such particles.

The experiments were carried out under the flow conditions which were described in detail earlier. [1].

After they had been put into the reactor, the samples were activated at $1\ 10^{-2}$ mm Hg pressure and 100°C for 24 hours. When the activation had been completed, the heating was discontinued and the vacuum replaced with pure hydrogen. The activity was measured in the pressure range 3-150 atm (gauge pressure) at 78, 64 and 22°K. The hydrogen flow rate through the reactor was varied between 50 and 240 liters/hr (calculated at N.T.P.) and the initial hydrogen contained 25% para-hydrogen.

Method of Calculation and Experimental Results

The reaction rate constants were calculated as before from the equation

$$k' = \frac{n_s}{Vc} \ln \frac{1 - C_0/C_b}{1 - C/C_e}.$$

Here k' is the reaction rate constant, mole/cm³·sec; n_s is the hydrogen input, mole/sec; V_c is the volume of catalyst in the reactor, cm³; C_0, C_e and C correspond to the initial and equilibrium concentrations and the concentration in the stream of p-H_2, %.

The values obtained for the reaction rate constants are given in Table 1.

TABLE 1

Values of k' (mole/cm³·sec) at Different Temperatures*

Hydroxide	$k' \cdot 10^3$		
	78° K (gas phase)	64° K (gas phase)	liquid phase
$Pr(OH)_3$	0,06—0,10	0,04—0,07	0,13—0,14
$Gd(OH)_3$	0,63—0,78	0,45—0,60	0,55—0,60
$Tb(OH)_3$	0,80—1,14	0,60—0,77	1,30—1,40
$Dy(OH)_3$	1,45—1,60	1,34—1,40	1,50—1,60

* The activity of different catalyst samples varies to a certain extent, but its maximum value is determined by the magnetic moment of the ion of the catalyst. Therefore in further discussions the maximum values of k' obtained (k'_{max}) has been used.

In the pressure range 3-150 atm no dependence of the rate constant on the pressure is observed.

The activation energies E at 78-64°K together with other characteristics have been determined and their values are given in Table 2.

Tables 1 and 2 show that in spite of the substantially large values of μ_{eff} for the rare earth element ions, their catalytic activity is lower than that of the iron group ions studied earlier [1].

Thus for Gr^{+++} and Mn^{++++} $\mu_{eff} = 3.87$, for Fe^{+++} $\mu_{eff} = 5.92$, and in these cases the reaction rate constants determined at 78°K are $0.74 \cdot 10^{-3}$, $1.2 \cdot 10^{-3}$ and $226 \cdot 10^{-3}$ respectively, which correspond to a value of k_{max}/μ^2_{eff} for the iron group of about 5-8, i.e. substantially higher than for the rare earth elements.

TABLE 2

Some Characteristics of the Hydroxides of the Rare Earth Elements as Catalysts

Characteristic	$Pr(OH)_3$	$Gd(OH)_3$	$Tb(OH)_3$	$Dy(OH)_3$
$\mu_{эф}$, μ_B [4]	3,62	7,94	9,70	10,6
ionic radius r' A° [3]	1,06—1,16	0,97—1,11	0,93—1,09	0,92—1,08
$k_{max} \cdot 10^5$(78°K)	0,767	1,23	1,22	1,42
$k_{22°K}/k_{78°K}$	1,68±0,12	1,0±0,04	1,35±0,15	1,02±0,04
E, cal/mole	200±50	80±30	100±30	80±30

This can be explained if one takes into account the fact that the radii of the iron group ions studied earlier are 0.60-0.74 A, i.e. rather smaller than the rare earth element ions. Since the value of the rate constant of Wigner's theory is inversely proportional to the sixth power of the shortest distance between the paramagnetic ion and a molecule of hydrogen (r), this slight difference in the values of r' leads to a considerable decrease in k'. The value of r does not always equal the distance during gas kinetic collisions, i.e. it is not known for certain. Therefore the change in catalytic activity of the ion in relation to its radius can only be calculated approximately.

In the present case the difference in radius of the ions with incomplete 3d and 4f electron shells is quite sufficient to explain the diminished activity of the latter.

The effect of the decrease in r with increasing charge of the nucleus is noticeable even within one group of elements, for example the four ions of the rare earth elements studied. With increasing nuclear charge the ionic radius r' decreases and the ratio k_{max}/μ^2_{eff} increases.

The results obtained lead to the conclusion that Wigner's theory, which was developed for homogeneous reaction conditions, is in reasonable agreement with the experimental material for the heterogeneous catalysis of this reaction on hydroxides.

Analysis of the material similarly leads to the following conclusion. Of all the known groups of elements with depleted inner electron shells (3d, 4d, 5d, 4f, and 5f) the minimum value of r' is observed for the elements in which the 3d shell is being filled. The values of all the groups of elements, with the exception of the rare earths (4f), does not exceed, and is usually considerably lower than, that of the iron group elements (3d). Therefore the ions of the iron group elements described earlier [1] can be considered the most active for the ortho-para-hydrogen conversion.

CONCLUSIONS

1. The catalytic activity and the ratio k_{max}/μ^2_{eff} have been determined for the hydroxides of the rare earth elements.

2. From the experimental and theoretical data a comparison of the catalytic activity has been made for the rare earth and iron group elements. The theoretical dependence of k' on μ_{eff} and r has been confirmed experimentally. It has been shown that Wigner's theory can be applied to heterogeneous catalysis in the case of magnetically dilute structures.

3. It has been shown that of all possible ions the most active for the conversion reaction should be the ions of elements with incomplete 3d electron shells. This conclusion has been confirmed experimentally.

In conclusion we would like to thank G. K. Boreskov, associate member of the Academy of Sciences SSSR, for his supervision of the work and valuable advice.

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All abbreviations of periodicals in the above bibliography are letter-by-letter transliterations of the abbreviations as given in the original Russian journal. *Some or all of this periodical literature may well be available in English translation.* A complete list of the cover-to-cover English translations appears at the back of this issue.

A NEW DESIGN OF PISTON FOR A GLASS CIRCULATION PUMP

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A new design of teflon piston is described.

The gas must circulate rapidly in the reaction space if measurements are made by means of flow methods; a pump circulates the gas. The pump is usually of piston type, in which the piston is moved magnetically; such a pump has a fairly high output (perhaps a few hundred liters per hour), does not contaminate the gas, and provides a means of adjusting the flow rate within certain limits.

The main fault in such pumps is that it is very difficult to obtain glassware of appropriate precision; gas leaks through any gap between the piston and cylinder, which makes the output low and complicates measurements of the flow rate. Moreover, the working parts become scratched and worn if a glass or metal piston is used, with the results that the output changes and that the piston may sieze up.

A mercury pump is free from the two latter disadvantages, but its output is usually small; moreover, mercury vapor enters the reaction space.

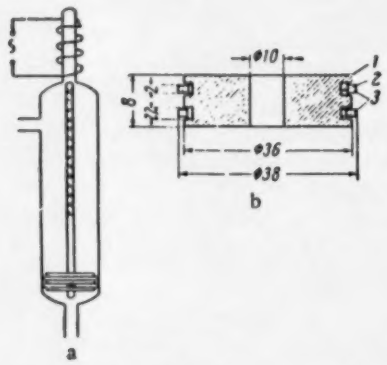

Fig. 1. a) General view of pump (without valves); b) Section of piston: 1) body; 2) stop; 3) ring.

We have used a glass barrel in conjunction with a teflon (PTFE) piston and teflon piston rings. This material has a very low coefficient of friction against glass. The split rings have an outside diameter greater than the diameter of the body; the gaps in the rings are located on opposite sides and the rings are prevented from rotating. The body has a diameter such that it enters the barrel freely; the rings provide the seal by pressing against the barrel (see Fig. 1). Considerable latitude is permissible on the diameter of the barrel, the leak is slight, and the output is constant.

We have used such a pump in a system having a considerable internal resistance. The magnetic field was switched on twice per second and provided an output of 600 liter/hr for a stroke of 120 mm(450 for 90 mm, 320 for 70 mm).

The pump may also be used at pressures below atmospheric.

THE SECOND INTERNATIONAL CONGRESS ON CATALYSIS

G. K. Boreskov and A. I. Gorbunov

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This congress was held in Paris on July 4-9, 1960; there were 846 participants from 31 countries, including 243 from France, 209 from the USA, 67 from Great Britain, and 41 from the USSR. There were 11 survey papers (given at the plenary sessions) and 144 research papers, which were read in three sections operating simultaneously: 60 in section 1 (on kinetics and mechanisms), 58 in section 2 (physicochemical aspects of catalysts and catalytic activity), and 26 in section 3 (applied catalysis).

The papers were distributed according to sources as follows: USA 44, USSR 20, France 14, Great Britain 12, Japan 10, Holland nine, Poland seven, Czechoslovakia, Italy, and West Germany five each, India and the Union of South Africa two each, and one each for Norway, East Germany, United Arab Republic, Belgium, Israel, Hungary and Turkey.

The section papers were preprinted and distributed; only five minutes were allowed for a summary of the main results and conclusions of each paper.

Most of the time in the sections was devoted to discussion.

The congress opened with an address from Professor Prêtre (France), the president of the executive committee; the chairmen were Campbell (Gt. Britain, section 1), Schwab (West Germany, section 2), and Hensel (USA, section 3).

Seven survey papers were presented at the plenary sessions on subsequent days.

Professor Voevodskii presented on behalf of Professor Semenov and himself a paper on chain reactions and chain mechanisms in heterogeneous reactions; this paper aroused much interest.

Natta (Italy) dealt with stereospecific catalysis in his detailed review of polymerization mechanisms for olefins, diolefins, aldehydes, etc. This method has provided new classes of crystalline macromolecular compounds, some of which are analogous to natural materials (polydiolefins of 1,4 structure), while others are entirely new (macromolecular hydrocarbons with isotactic, syndiotactic, and diisotactic structures). Ionic coordination mechanisms were discussed in relation to the conditions that determine whether a cationic or anionic mechanism is operative.

Bell (Gt. Britain) dealt with the theory of kinetic isotope effects in relation to acid-base catalysis in his paper on hydrogen-isotope effects in acid-base catalysis.

This effect has been used to elucidate the enolization of acetone in the presence of acetic acid and acetate ions.

A rigorous theory of the effect (with allowance for tunneling was presented to explain some experimental results that were in conflict with earlier theories.

This paper is of considerable interest in relation to homogeneous catalysis.

Theorell (France) dealt with enzymatic catalysis and demonstrated clearly that it has much in common with ordinary catalysis. Recent progress in enzymology has important consequences for the general theory of catalysis. Very interesting results were presented on the intermediate complexes formed by enzymes and coenzymes.

Heineman (USA) dealt with the relation between fundamental and applied studies on catalysis; his rather pessimistic view was that for 70 years all the important discoveries in applied catalysis have derived very largely from empirical studies. Fundamental work on theory and mechanisms lags behind practical uses. In his opinion, the basic reason for this is that the theoretical studies are divorced from chemical reactions and come even closer to studies in solid state physics. A further reason is that insufficient effort is devoted to theoretical research.

Concentrated work on the theory is required; this may best be achieved by setting up special institutes resembling Professor Prêtre's in France. He urged other countries to follow this example.

The first part of the paper by Gudrey (USA) was a review of the introduction of catalysts into industrial processes, which at first were used in simple inorganic systems but later were introduced into organic systems.

The second part dealt with the main future trends, of which he considered one of the most important to be the protection of health by means of catalytic after-combustion of automobile exhaust gases in order to minimize contamination from harmful compounds (including carcinogenic ones); other such applications are to the removal of bacteria and viruses in air conditioning. Catalysis is also important in oil refining and will undoubtedly have a very close relation with enzymology.

A future problem will be to make catalysts better than those found in plants and animals.

H. Taylor (USA) summed up the work of the congress in his address to the last plenary session. He pointed out that the mechanisms of some classical catalyzed reactions are still not fully understood; fresh studies by modern methods are required. He instanced the production of ammonia; the Temkin mechanism, long hitherto generally accepted, had now fallen into disrepute. He emphasized the high standard of the papers on formic acid that had been presented, the importance of the work of Solbaken (Norway) on the transmission coefficient in heterogeneous kinetics, and the significance of the work of Boreskov and Vasilevich (USSR) on isotope exchange on platinum films.

He expressed his expectation of future progress in the field of stereospecific polymerization, which was inadequately represented at the congress. He anticipated that this field would form the main theme of a future congress on catalysis.

These addresses all dealt with very interesting problems, but they did not include one on the more important features of the theory, namely the selection of catalysts, the relation of activity to the physical parameters of the catalyst, the kinetic laws of catalyzed reactions, and so on. In consequence, no proper general discussion of these topics was possible.

The sectional papers are too numerous for each one to be considered. The papers had not been assigned to the sections with proper care; papers with similar subjects were often in different sections.

Section 1 was concerned with mechanisms and kinetics.

Some 35 of the papers dealt with particular heterogeneous reactions; results were usually given on the formal kinetics, from which deductions as to the mechanism were made.

Simple model reactions were used in much of this work (isotope exchange, decomposition of formic acid, hydrogenation and dehydrogenation of simple hydrocarbons). Not much use has been made of circulation methods, which are now extensively used in the USSR.

The papers on the general features of reaction kinetics included one by Horiuti (Japan) on his statistical method as applied to hydrogenations.

Solbaken dealt with the fundamental topic of the transmission coefficient. It is often assumed that the reaction in an adsorption process is adiabatic, with a transmission coefficient close to one, but this is not so in every case, as Solbaken showed for the adsorption of NO on alumina gel (transmission coefficient 10^{-8}). It is usual to explain the small pre-exponential factors in the rate constants for adsorption in terms of low entropy in the transition complex; Solbaken considers that low transmission coefficients are a more likely cause in some cases.

Weiss (USA) dealt with methods applicable to the formal kinetics of many-stage reactions, in particular those of hydrocarbons.

Nine papers were devoted to homogeneous reactions such as chlorination of aromatic amines, decomposition of hydrogen peroxide, gas-phase isomerization of butene, etc. Interest in the theory of homogeneous catalysis appears to be increasing, especially abroad.

Balandin (USSR) dealt with the multiplet theory in relation to the rational choice of a catalyst. He gave new results on the effects of molecular structure on reactivity.

Schuit, van Rein, and Zachtler (Holland) considered the relation of the catalytic activity of a metal to the heats of formation of appropriate compounds (oxides, hydrides, etc.) and to the estimated stability of transition complexes.

Makishima, Ioden, and Saito (Japan) presented a similar but more general and elementary treatment of the subject.

Balaceanu and Joney (France) showed that a catalyst which can accelerate the oxidation of hydrogen and the dehydrogenation of hydrocarbons can be used to perform oxidative dehydrogenation at temperatures too low for simple catalytic dehydrogenation to be possible.

There were several papers on adsorption processes, which included some highly original treatments. Sweet and Rideal (Gt. Britain) used a very high vacuum (10^{-10} mm Hg) to measure the heat and entropy of adsorption of hydrogen on nickel for a wide range of degrees of saturation (0.005-0.8); on this basis they deduced the degree of localization of the hydrogen as a function of the saturation.

Nasini and others (Italy) have used similar methods in studies of nitrogen and carbon monoxide adsorbed in tungsten at 10^{-7} to 10^{-8} mm Hg; their results for nitrogen differ greatly from those of Baker et al. In this connection Dell (USA) pointed out in the discussion that allowance must be made for dissociation at the heated tungsten filament under these conditions. Fisher, Tomezko, and Aston (USA) have used a special method of removing gases from platinum black in the cold; the firmly bound hydrogen (or oxygen) is converted to water, which is readily taken up by a cold trap. Tamaru gave some interesting results on the marked effect of hydrogen on the rate of adsorption of nitrogen on a doubly promoted iron catalyst used in ammonia synthesis. These results are very much in conflict with the literature, as Scholten (Holland) and Gorbunov (USSR) pointed out in the discussion.

Kim and Krieger (USA) have examined the cyclization of n-heptane during the formation of a chromic oxide catalyst.

Section 2 was concerned with the activity and physicochemical properties of catalysts. This was the section with the greatest attendance.

There were many papers on the electronic structures of solid catalysts. Dowden and Wells (Gt. Britain) extended Dowden's theory of the unfilled d levels by means of the theory of the crystalline field; here attention was directed to the electron structure of the cations in the solid, and a general treatment of heterogeneous and homogeneous catalysis was proposed on this basis. This development, although as yet not fully worked out, is of great interest.

Cox (USA), Dalgliesh (Gt. Britain), and Grey (USA) presented new evidence for the importance of holes in the d-shells.

Nasini showed that there is a rather complicated relation between the activity of a film of vacuum-evaporated metal and the nature of the metal; this relation is not explained by the d-shell theory, even if allowance is made for possible effects from the lattice parameter of the film.

There were several papers on catalysts as semiconductors, e.g. those by Roginskii (USSR), Vol'kenstein (USSR), Grey, Beljanski (Poland), Treszozanovicz (Poland), and Smith (USA).

A paper by Simino (Italy) in section 1 dealt also with this topic in relation to the chemisorption of hydrogen on zinc oxide containing Ga_2O_3 or li_2O.

Szabo and Szolumozy (Hungary) have found that the carrier (TiO_2 or Cr_2O_3) has a marked effect on the activity of nickel in the decomposition of formic acid.

The only electrical measurement made in most cases is that of the conductivity.

The semiconductor theory was not the center of attention at the congress, as was shown by the contributions made to the discussion by Dowden, Emmett, Zachtler, Schwab, and others; most of the participants placed emphasis on the *d*-shell theory.

Several papers dealt with catalysts (principally aluminosilicates) for acid-base reactions.

There were five papers on the effects of radiation on solid catalysts, namely one by Balandin and others on β rays from calcium and sulfur on magnesium sulfate as a catalyst for the dehydration of cyclohexanol, one by Haissinsky (France) on the effects of γ rays on platinum and numerous oxides and salts, one by Barry (Gt. Britain) on the effects of γ rays (USA) on the effects of radiation on silica gel as a catalyst for the H_2+O_2 reaction, and one by Romero-Rossi and Stone (Gt. Britain) on the effects of ultraviolet light on the oxidation of CO on zinc oxide.

Much of this work is on its early stages, but it provoked a lively discussion.

Several papers on sepcific catalytic activity were presented; the activity is often nearly independent of the method of preparation, as Nikolaenko et al. (Czechoslovakia) demonstrated for Ni-MgO (hydrogenation of benzene); Dell, Hess, and Wheeler (USA) have done the same for magnesium oxide as a catalyst for the decomposition of nitric oxide, and Dutch workers for the conversion of carbon monoxide on iron oxide.

Topchieva (USSR) considered the relation of porosity to catalytic activity.

Rubinshtein (USSR) presented a detailed study of potassium-chromium alumina catalysts.

Highly active contact catalysts can be prepared from materials other than the metals, oxides, and sulfides usually used; Changfoot and Sabb (South Africa) demonstrated that the monosulfides of the transition elements in period four will catalyze the decomposition of ammonia, while Sandler (USA; section 1) showed that silicides such as $MoSi_2$ and VSi_2 are highly active as regards the H_2+O_2 reaction (molybdenum silicide is active even at liquid nitrogen temperature).

The number and standard of the papers in section 3 (applied catalysis) did not provide a proper indication of the situation in this branch of the subject. Recent progress in many fields was not represented (e.g. production of monomers, polymerization, the search for the best conditions, etc.). The research divisions of major companies took no active part in the congress; most of the foreign papers were given by workers from educational institutions.

There were only two papers on the theory of industrial catalysts, namely that by Panchenkov (USSR) on the kinetics of heterogeneous reactions in flow systems and that by Slin'ko (USSR) on the stability limits of exothermic contact processes.

Souriradjan (India) dealt with the oxidation of hexane at low concentrations over a catalyst consisting of vanadium pentoxide or copper oxide on aluminum oxide or kieselguhr; Vetch (USA) dealt with the oxidation of propylene to acrolein over a new catalyst, whose active component has the empirical formula $Bi_9PMo_{12}O_{52}$.

Fabus (Canada) demonstrated that TiO_2 and SnO_2 increase the activity of vanadium pentoxide by a factor of 1.6 in relation to the oxidation of napthalene to phthalic anhydride.

Kerby (USA) described a new catalyst consisting of $AlPO_4$ and having a specific surface of 400 m^2/g.

Petrov (USSR) described catalytic syntheses of organosilicon compounds, together with some polymerization reactions.

Shuikin and Bel'skii (USSR) dealt with the hydrogenation and hydrogenolysis of furanes containing side-chain hydroxyl, carbonyl, carboxyl, and other groups. Sokol'skii and Shmonina (USSR) dealt with the kinetics and mechanisms of catalyzed reductions of aromatic nitro compounds.

Stanfield and Robbins (USA) reported detailed and systematic studies of a skeletal copper hydrogenation catalyst.

Zabor (USA) dealt with the direct production of ethanol from ethylene over blue tungsten oxide (close to W_2O_5 in composition).

Mamedaliev and Guseinov (USSR) reported on the chlorination of hydrocarbons, and Battachuri and Ganguli

(India) described the productions of butadiene from alcohol, both by means of fluidized beds. The latter obtained yields of useful products exceeding the theoretical values, probably on account of errors of technique.

There were several papers on processes based on carbon monoxide.

Murakami and Shiba (Japan) gave some interesting results on the synthesis of acetonitrile from acetylene and ammonia; aluminum oxide promoted by alkali metals can give yields up to 99%.

No essentially new methods were described, but comparatively new methods (infrared spectrometry, electron spin resonance, nuclear magnetic resonance, isotope methods, high vacuum techniques) are becoming standard in many foreign laboratories.

Magnetic methods (eight papers) have been used to study binding in adsorption as well as to establish the composition and grain size of a catalyst; Selwood (USA) gave an interesting paper on the measurement of the number of bonds to the surface formed by adsorbed hydrogen, hydrogen sulfide, ethylene and benzene.

Electron spin resonance (FSR) has recently been used in this connection for the first time in relation to the states of oxides of chromium in polymerization and dehydrogenation catalysts by Cosse and van Rein, and by Pecherskaya, Kazanskii, and Voevodskii (USSR).

Turkevich et al (USA) have made ESR studies of charcoal and also have made NMR studies of water adsorbed on aluminosilicate catalysts.

Infrared spectroscopy has been used to advantage, e.g. by Terenin and Roev (USSR); other important uses were those reported by Eyshens and Pliskin (USA) for the decomposition of formic acid and by Leftin and Hull (USA) for saturated hydrocarbons chemisorbed on aluminosilicate catalysts.

New uses have been found for isotope methods. Boreskov and Vasilevich have used deuterium and tritium to deduce the type of inhomogeneity to be found on platinum; they have used kinetic isotope techniques to deduce the exchange mechanism applicable to low temperatures. Campbell (Gt. Britain) reported on the use of isotope exchange to elucidate dissociative adsorption of organic compounds on metals. Roiter (USSR) has used oxygen isotopes to examine oxidation mechanisms for oxide catalysts.

High-vacuum techniques are much used in adsorption studies; Baker (USA) has used them to examine the effects of hydrogen on the work function of the faces of tungsten crystals.

Soviet delegates took an active part in all sections.

Papers not appearing in the original program were presented: one by Klabunovskii on stereospecific catalysis, one by Lyubarskii on the specific activity of nickel hydrogenation catalysts, and one by Krylov on some principles for selecting semiconductor catalysts.

A serious disadvantage was that Russian was not one of the working languages of the congress.

Organization was discussed at one of the plenary sessions; the organizational arrangements will have to be revised. At present the council of directors has nine members, all of whom are nationals of the USA. This situation is so anomalous that the council itself proposed that four further directors from other countries should be appointed; this proposal would produce no real change, so the Soviet delegation proposed that the congress should be reorganized as a proper international organization affiliated to Unesco, after which the controlling body should be appointed in accordance with the proper representation of the various countries. This proposal received overwhelming support at the subsequent voice vote and was adopted.

At the same session it was resolved to hold the Third International Congress on Catalysis in Holland in 1964.

The second congress was the largest meeting of workers in this field; there were present many of the leading authorities from 31 countries, who presented more than 150 papers.

The personal contacts, discussions on research methods, exchanges of view, and the understanding that resulted, must all contribute greatly to future progress in this field.

The material presented at the congress should be of great value to all who work in this field in the USSR.

INTERNATIONAL SYMPOSIUM ON THE CHEMISTRY OF MACROMOLECULES

A. A. Arest-Yakubovich and Kh. S. Bagdasaryan

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Original article submitted September 5, 1960

This symposium was organized by the International Union of Pure and Applied Chemistry and was held in Moscow on June 14-18, 1960. The three main topics were polymer synthesis, polymerization and polycondensation processes, and chemical reactions in polymers.

Over 170 papers were read; this report deals only with papers on polymerization catalysts and the kinetics and mechanisms of polymerization processes.

Three papers were given at the plenary sessions.

H. Mark (USA) dealt with syntheses, properties, and uses of new polymers. P. Doty (USA) dealt with molecular biology under the title "Polynucleotides and nucleic acids".

N. N. Semenov dealt with collective interactions in polymerization processes and in polymers with conjugated bonds; his treatment covered low-temperature and solid-state polymerization processes. In some cases such processes proceed rapidly and have low activation energies. He proposed as a working hypothesis that a radical in the solid state can link at one step to a large group of monomer molecules, which have previously become suitably aligned in the crystal. A description was given of the properties of polymers having conjugated bond systems; such polymers conduct electricity, give ESR signals, and catalyze certain redox reactions.

Interest in radical polymerization at present centers on the details of the elementary processes and on the quantitative aspects of reactions involving polymer radicals. Bresler, Kazbekov, and Saminskii (USSR) dealt with the chemical behavior of the radicals produced from vitrified polymers ruptured mechanically under vacuum. The ESR spectra have been used to follow the destruction of these radicals by reaction with oxygen or with hydrogen donors. Bagdasar'yan and Sinitsyna (USSR) have used inhibitors to measure the reaction constants of the polymer radicals formed by vinyl acetate, methyl acrylate, and acrylonitrile with various aromatic compounds. It has been found that the inhibition constant is related to the structure of the inhibitor. Tudesz, Kende, and Azory (Hungary) have used derivatives of trinitrobenzene as inhibitors for the polymerization of styrene. Bamford and Jenkins (Gt. Britain) proposed a new way of describing the polarity effect in radical reactions. Wolling (USA) has studied chain initiation, propagation, transfer, and termination at pressures up to 10,000 atm.

Razuvaev et al (USSR) were among those who presented papers on topics related to radical polymerization; they reported on the thermal decomposition of some peranhydrides and peresters, which can act as polymerization initiators. Delsen and Smuts (Belgium) described the polymerization of aqueous acrylamide as initiated by peroxy radicals generated photochemically in a redox system containing a dye (e.g. eosin), ascorbic acid, and oxygen. Bernat and Bodarat (France) and Due and Orbizo (Belgium) discussed radiation-induced polymerization.

There were over 20 papers on ionic and stereospecific polymerization. Gee et al (Gt. Britain) reported on styrene used with sodium and naphthalene in dioxane; the Szwarc mechanism was confirmed. Medvedev et al (USSR) dealt with the kinetics and mechanisms of processes induced by organolithium compounds (isoprene or

styrene in toluene-trimethylamine mixtures); Korotkov et al (USSR) did the same for methyl methacrylate in toluene. Parrot and Beynere (France) reported on the use of inclusion compounds of graphite, $(C_3K)_n$ and $(C_{24}K)_n$, as catalysts for the polymerization of styrene, butadiene, and isoprene. Vesely (Czechoslovakia) dealt with cationic polymerization as studied in terms of the electrical conductivity of the system. In some cases free ions (not ion pairs) are involved. Zlamal and Kazda (Czechoslovakia) showed that some nonpolar compounds (e.g. benzene and hexane) differ in respect of their effects on the cationic polymerization of isobutene. Kern and Jax (W. Germany) dealt with some effects in the cationic polymerization of trioxane.

Mazzanti (on behalf of Natta, Italy) reported on recent work on stereospecific polymerization; synthesis conditions and structures were reported for many new stereoregular polymers derived from butadiene, aldehydes, acrylates, and 2-vinylpyridine; results were also given on polymerizations effected by catalysts such as aluminum and beryllium amides in conjunction with $TiCl_3$. Anion-coordination and cation-coordination types of polymerization were differentiated. Huggins (USA) and Bresler et al.(USSR) dealt with the processes on stereospecific catalysts. Bocek (Czechoslovakia)reported on the polymerization of propylene on catalysts consisting of $Al(C_2H_5)_3$ and mixed crystals of $TiCl_3$ or $TiCl_2$ withhalidesof the metals of groups two to eight (these halides are produced when $TiCl_4$ is reduced by the metals). Erusalimskii et al.(USSR) demonstrated that the structures of polyisoprene and polybutadiene produced by $C_4H_9MgI+(C_4H_9)_2Mg+TiCl_4$ catalysts are controlled to a large extent by the composition of the catalyst. Kargin and Platé showed that many crystalline substances acquire the ability to initiate polymerizations when they are ground up. The mechanism of the process depends on the nature of the solid and on the nature of the monomer.

Several papers were concerned with solid-state and radiation-induced polymerizations. Bamford, Jenkins, and Ward (Gt. Britain) reported on the photopolymerization of crystalline methacrylic acid and on the radicals produced in high-frequency discharges. Adler, Ballantyne, and Beizal (USA) described the radiation-induced polymerization of solid acrylamide. The ESR spectrum and polarizing-microscope patterns were used to show that the process is not homogeneous (polymer regions develop gradually from nuclei). The radicals so produced persist for many months.

Magat et al.(France) described the polymerization of formaldehyde between -196° and -80° as induced by gamma rays; they found that the over-all activation energy falls discontinuously as the liquid solidifies (the rate of polymerization also increases sharply). Kargin and Kabanov (USSR) gave some interesting results on solid-state polymerization near the melting point for insoluble compounds present in very finely divided form. Benzasson and Marks (France) and Volokhina et al.(USSR) also dealt with aspects of solid-state polymerization.

Magat (France) gave an extensive review of radiation-induced polymerization and of the effects of radiation on polymers. Abkin et al.(USSR) reported on low-temperature radiation-induced polymerization; they found that carbonium and carbanion mechanisms are both possible.

There were also many papers on the preparation and properties of new polymers and on the reactions of polymer chains.

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Soviet Journals Available in Cover-to-Cover Translation

ABBREVIATION	RUSSIAN TITLE	TITLE OF TRANSLATION	PUBLISHER	TRANSLATION BEGAN Vol.	Issue	Year
AÉ	Atomnaya énergiya	Soviet Journal of Atomic Energy	Consultants Bureau	1	1	1956
Akust. zh.	Akusticheskii zhurnal	Soviet Physics – Acoustics	American Institute of Physics	1	1	1955
	Antibiotiki	Antibiotics	Consultants Bureau	4	1	1959
Astr(on). zh(urn).	Astronomicheskii zhurnal	Soviet Astronomy–AJ	American Institute of Physics	34	1	1957
Avto(mat). svarka	Avtomaticheskaya svarka	Automatic Welding	British Welding Research Association (London)		1	1959
	Avtomatika i Telemekhanika	Automation and Remote Control	Instrument Society of America	27	1	1956
	Biofizika	Biophysics	National Institutes of Health*		1	1957
	Biokhimiya	Biochemistry	Consultants Bureau	21	1	1956
Byull. éksp(erim). biol. i med.	Byulleten' éksperimental'noi biologii i meditsiny	Bulletin of Experimental Biology and Medicine	Consultants Bureau	41	1	1959
DAN (SSSR) / Dokl(ady) AN SSSR	Doklady Akademii Nauk SSSR	The translation of this journal is published in sections, as follows:				
		Doklady Biochemistry Section	American Institute of Biological Sciences	106	1	1956
		Doklady Biological Sciences Sections (Includes: Anatomy, biophysics, cytology, ecology, embryology, endocrinology, evolutionary morphology, genetics, histology, hydrobiology microbiology, morphology, parasitology, physiology, zoology sections)	American Institute of Biological Sciences	112	1	1957
Life Sciences		Doklady Botanical Sciences Sections (Includes: Botany, phytopathology, plant anatomy, plant ecology, plant embryology, plant physiology, plant morphology sections)	American Institute of Biological Sciences	112	1	1957
		Proceedings of the Academy of Sciences of the USSR, Section: Chemical Technology	Consultants Bureau	106	1	1956
Chemical Sciences		Proceedings of the Academy of Sciences of the USSR, Section: Chemistry	Consultants Bureau	106	1	1956
		Proceedings of the Academy of Sciences of the USSR, Section: Physical Chemistry	Consultants Bureau	112	1	1957
		Doklady Earth Sciences Sections (Includes: Geochemistry, geology, geophysics, hydrogeology, mineralogy, paleontology, petrography, permafrost sections)	American Geological Institute	124	1	1959
Earth Sciences		Proceedings of the Academy of Sciences of the USSR, Section: Geochemistry	Consultants Bureau	106-123	1-6	1957-1958
		Proceedings of the Academy of Sciences of the USSR, Sections: Geology	Consultants Bureau	106-123	1-6	1957-1958
Mathematics		Doklady Soviet Mathematics	The American Mathematics Society	131	1	1961
		Soviet Physics–Doklady (Includes: Aerodynamics, astronomy, crystallography, cybernetics and control theory, electrical engineering, energetics, fluid mechanics, heat engineering, hydraulics, mathematical physics, mechanics, physics, technical physics, theory of elasticity sections)	American Institute of Physics	106	1	1956
Physics		Proceedings of the Academy of Sciences of the USSR, Applied Physics Sections (does not include mathematical physics or physics sections)	Consultants Bureau	106-117	1	1956-1957
Derevoobrabat. prom-st'.	Derevoobrabatyvayushchaya promyshlennost'	Wood Processing Industry	Timber Development Association (London)		9	1959
Élektrosvyaz		Telecommunications	Massachusetts Institute of Technology*		1	1957
Éntom(ol). oboz(renie)	Éntomologicheskoe obozrenie	Entomological Review	American Institute of Biological Sciences	38	1	1959
Farmakol. (i) toksikol(ogiya)	Farmakologiya i toksikologiya	Pharmacology and Toxicology	Consultants Bureau	20	1	1957
FMM	Fizika metallov i metallovedenie	Physics of Metals and Metallography	Acta Metallurgica*	5	1	1957
Fiziol. zhurn. SSSR (im. Sechenova)	Fiziologicheskii zhurnal im. I. M. Sechenova	Sechenov Physiological Journal USSR	National Institutes of Health*		1	1957
Fiziol(ogiya) rast.	Fiziologiya rastenii	Plant Physiology	American Institute of Biological Sciences	4	1	1957
	Geokhimiya	Geochemistry	The Geochemical Society		1	1958
FTT	Fizika tverdogo tela	Soviet Physics–Solid State	American Institute of Physics	1	1	1959
Izmerit. tekh(nika)	Izmeritel'naya tekhnika	Measurement Techniques	Instrument Society of America		1	1959
Izv. AN SSSR, O(td). Kh(im). N(auk)	Izvestiya Akademii Nauk SSSR: Otdelenie khimicheskikh nauk	Bulletin of the Academy of Sciences of the USSR: Division of Chemical Sciences	Consultants Bureau		1	1952

continued

Izv. AN SSSR, O(td). T(ekhn). N(auk): Met(all). i top.	(see Met. i top.)				
Izv. AN SSSR Ser. fiz(ich).	Izvestiya Akademii Nauk SSSR: Seriya fizicheskaya	Bulletin of the Academy of Sciences of the USSR: Physical Series	Columbia Technical Translations	1	1954
Izv. AN SSSR Ser. geofiz.	Izvestiya Akademii Nauk SSSR: Seriya geofizicheskaya	Bulletin (Izvestiya) of the Academy of Sciences USSR: Geophysics Series	American Geophysical Union	1	1954
Izv. AN SSSR Ser. geol.	Izvestiya Akademii Nauk SSSR: Seriya geologicheskaya	Izvestiya of the Academy of Sciences of the USSR: Geologic Series	American Geological Institute	1	1958
Kauch. i rez.	Kauchuk i rezina	Soviet Rubber Technology	Research Association of British Rubber Manufacturers	18	1 1959
	Kinetika i kataliz	Kinetics and Catalysis	Consultants Bureau	1	3 1960
	Koks i khimiya	Coke and Chemistry USSR	Coal Tar Research Association (Leeds, England)		1 1958
Kolloidn. zh(urn).	Kolloidnyi zhurnal	Colloid Journal	Consultants Bureau	14	1 1952
	Kristallografiya	Soviet Physics – Crystallography	American Institute of Physics	2	1 1957
Metalov. i term. obrabot. metal.	Metallovedenie i termicheskaya obrabotka metallov	Metal Science and Heat Treatment of Metals	Acta Metallurgica	6	1 1958
	Metallurg	Metallurgist	Acta Metallurgica		1 1957
Met. i top.	Metallurgiya i topliva	Russian Metallurgy and Fuels	Eagle Technical Publications		1 1960
Mikrobiol.	Mikrobiologiya	Microbiology	American Institute of Biological Sciences	26	1 1957
OS	Optika i spektroskopiya	Optics and Spectroscopy	American Institute of Physics		6 1959
	Pochvovedenie	Soviet Soil Science	American Institute of Biological Sciences		1 1958
	Priborostroenie	Instrument Construction	British Scientific Instrument Research Association		1 1959
Pribory i tekhn. éks(perimenta)	Pribory i tekhnika éksperimenta	Instruments and Experimental Techniques	Instrument Society of America		1 1957
Prikl. matem. i mekh.	Prikladnaya matematika i mekhanika	Applied Mathematics and Mechanics	American Society of Mechanical Engineers		1 1958
PTÉ	(see Pribory i tekhn. éks.)				
	Problemy Severa	Problems of the North	National Research Council of Canada		
Radiotekh.	Radiotekhnika	Radio Engineering	Massachusetts Institute of Technology*	12	1 1957
Radiotekh. i élektronika	Radiotekhnika i élektronika	Radio Engineering and Electronics	Massachusetts Institute of Technology*	2	1 1957
	Stanki i instrument	Machines and Tooling	Production Engineering Research Assoc.		1 1959
	Stal'	Stal (In English)	Iron and Steel Institute		1 1959
Stek. i keram.	Steklo i keramika	Glass and Ceramics	Consultants Bureau	13	1 1956
Svaroch. proiz-vo	Svarochnoe proizvodstvo	Welding Production	British Welding Research Association		4 1959
Teor. veroyat. i prim.	Teoriya veroyatnostei i ee primenenie	Theory of Probability and Its Applications	Society for Industrial and Applied Mathematics		1 1956
Tsvet. Metally	Tsvetnye metally	Nonferrous Metals	Primary Sources		1 1960
UFN	Uspekhi fizicheskikh Nauk	Soviet Physics – Uspekhi (partial translation)	American Institute of Physics	66	1 1958
UKh	Uspekhi khimii	Russian Chemical Reviews	The Chemical Society (London)		1 1960
UMN	Uspekhi matematicheskikh nauk	Russian Mathematical Surveys	London Mathematical Society	15	1 1960
Usp. fiz. nauk	(see UFN)				
Usp. khim(ii)	(see UKh)				
Usp. matem. nauk	(see UMN)				
Usp. sovr. biol.	Uspekhi sovremennoi biologii	Russian Review of Biology	Oliver and Boyd	48	1959
Vest. mashinostroeniya	Vestnik mashinostroeniya	Russian Engineering Journal	Production Engineering Research Assoc.	4	1959
Vop. gem. i per. krovi	Voprosy gematologii i perelivaniya krovi	Problems of Hematology and Blood Transfusion	National Institutes of Health*	1	1957
Vop. onk.	Voprosy onkologii	Problems of Oncology	National Institutes of Health*	1	1957
Vop. virusol.	Voprosy virusologii	Problems of Virology	National Institutes of Health*	1	1957
Zav(odsk). lab(oratoriya)	Zavodskaya laboratoriya	Industrial Laboratory	Instrument Society of America	25	1 1959
ZhAKh Zh. anal(it). khimii	Zhurnal analiticheskoi khimii	Journal of Analytical Chemistry USSR	Consultants Bureau	7	1 1952
ZhETF Zh. éksperim. i teor. fiz.	Zhurnal éksperimental'noi i theoreticheskoi fiziki	Soviet Physics–JETP	American Institute of Physics	28	1 1955
ZhFKh Zh. fiz. khimii	Zhurnal fizicheskoi khimii	Russian Journal of Physical Chemistry	The Chemical Society (London)		7 1959
ZhMÉI Zh(urn). mikrobiol. épidemiol. i immunobiol.	Zhurnal mikrobiologii, épidemiologii i immunobiologii	Journal of Microbiology, Epidemiology and Immunobiology	National Institutes of Health*		1 1957
ZhNKh Zh(urn). neorgan(ich). khim(ii)	Zhurnal neorganicheskoi khimii	The Russian Journal of Inorganic Chemistry	The Chemical Society (London)		1 1959
ZhOKh Zh(urn). obshch(ei) khimii	Zhurnal obshchei khimii	Journal of General Chemistry USSR	Consultants Bureau	19	1 1949
ZhPKh Zh(urn). prikl. khimii	Zhurnal prikladnoi khimii	Journal of Applied Chemistry USSR	Consultants Bureau	23	1 1950
ZhSKh Zh(urn). strukt. khimii	Zhurnal strukturnoi khimii	Journal of Structural Chemistry	Consultants Bureau	1	1 1960
ZhTF Zh(urn). tekhn. fiz.	Zhurnal teknicheskoi fiziki	Soviet Physics–Technical Physics	American Institute of Physics	26	1 1956
Zh(urn). vyssh. nervn. deyat. (im. Pavlova)	Zhurnal vysshei nervnoi deyatel'nosti (im. I. P. Pavlova)	Pavlov Journal of Higher Nervous Activity	National Institutes of Health*		1 1958

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SIGNIFICANCE OF ABBREVIATIONS MOST FREQUENTLY ENCOUNTERED IN SOVIET PERIODICALS

FIAN	Phys. Inst. Acad. Sci. USSR.
GDI	Water Power Inst.
GITI	State Sci.-Tech. Press
GITTL	State Tech. and Theor. Lit. Press
GONTI	State United Sci.-Tech. Press
Gosenergoizdat	State Power Press
Goskhimizdat	State Chem. Press
GOST	All-Union State Standard
GTTI	State Tech. and Theor. Lit. Press
IL	Foreign Lit. Press
ISN (Izd. Sov. Nauk)	Soviet Science Press
Izd. AN SSSR	Acad. Sci. USSR Press
Izd. MGU	Moscow State Univ. Press
LEIIZhT	Leningrad Power Inst. of Railroad Engineering
LET	Leningrad Elec. Engr. School
LETI	Leningrad Electrotechnical Inst.
LETIIZhT	Leningrad Electrical Engineering Research Inst. of Railroad Engr.
Mashgiz	State Sci.-Tech. Press for Machine Construction Lit.
MEP	Ministry of Electrical Industry
MES	Ministry of Electrical Power Plants
MESEP	Ministry of Electrical Power Plants and the Electrical Industry
MGU	Moscow State Univ.
MKhTI	Moscow Inst. Chem. Tech.
MOPI	Moscow Regional Pedagogical Inst.
MSP	Ministry of Industrial Construction
NII ZVUKSZAPIOI	Scientific Research Inst. of Sound Recording
NIKFI	Sci. Inst. of Modern Motion Picture Photography
ONTI	United Sci.-Tech. Press
OTI	Division of Technical Information
OTN	Div. Tech. Sci.
Stroiizdat	Construction Press
TOE	Association of Power Engineers
TsKTI	Central Research Inst. for Boilers and Turbines
TsNIEL	Central Scientific Research Elec. Engr. Lab.
TsNIEL-MES	Central Scientific Research Elec. Engr. Lab.–Ministry of Electric Power Plants
TsVTI	Central Office of Economic Information
UF	Ural Branch
VIESKh	All-Union Inst. of Rural Elec. Power Stations
VNIIM	All-Union Scientific Research Inst. of Metrology
VNIIZhDT	All-Union Scientific Research Inst. of Railroad Engineering
VTI	All-Union Thermotech. Inst.
VZEI	All-Union Power Correspondence Inst.

Note: Abbreviations not on this list and not explained in the translation have been transliterated, no further information about their significance being available to us. – Publisher.